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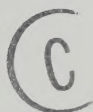
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THE UNIVERSITY OF ALBERTA

CRYSTAL STRUCTURES OF SOME ALICYCLIC COMPOUNDS
AND AN IRON COMPLEX

by



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A THESIS

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ABSTRACT

A brief summary of the crystallographic method is given, with the emphasis upon the methods used for phase determination.

The crystal structure of bis-nitrosyl-tris-1,2-diphenyl dithiolene diiron was determined. An unusual asymmetric bridging mode of the dithiolene ligand, was found to be responsible for the observation of two iron sites in the Mössbauer spectrum of the compound. There was no evidence of coordination with solvent, as had been suggested by one author. It is suggested that this type of bridging may be present in several other transition metal dithiolene complexes.

The conformation of cyclohexa-1,4-diene has been a controversial topic. The crystal structure of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene was determined to provide additional evidence concerning the planarity of the ring system. This molecule was found to be almost planar, but with significant deviations from planarity leading to a slight chair conformation. It appears that repulsive interaction between the bulky substituents is responsible for this chair conformation.

The crystal structure of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo[3.1.0.^{2,4}0]hexane was carried out to determine the exact stereochemistry of the molecule and to obtain precise structural information on the cyclopropane and cyclobutane rings in highly strained fused systems. The molecule was found to be the *anti* configuration with the carbo-

methoxy groups in the *exo* position. The molecule exhibits an unusual feature in that all the bond lengths within the tricyclic framework are equal. The bond lengths in the cyclopropane rings are longer than in cyclopropane itself and those in the cyclobutane ring are shorter than in cyclobutane. A discussion of the geometry of cyclopropane and cyclobutane rings in fused systems is given.

In the preparation of *exo*-tricyclo[3.1.1.0^{2,4}]hept-6-yl-acetate by addition of carbene to *exo*-bicyclo[2.1.1]-hex-2-ene-5-yl acetate only one isomer is formed. The X-ray crystal structure of the *p*-bromobenzoate derivative revealed that this is the isomer in which the cyclopropane ring is *anti* with respect to the bridgehead carbon bearing the *p*-bromobenzoate group. Structural evidence is provided to support the view that the hydrogen on C5 of the bicyclohexene derivative sterically interferes with the formation of the *syn* isomer.

An appendix gives a criticism of the structure determination of WOF₄ and describes an attempt to refine it in terms of a disordered model.

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CRYSTALLOGRAPHIC INTRODUCTION

Crystal Lattice

A crystal may be regarded as a body consisting of a regular repetition in space of identical units. The repetition is along three axes x , y , z , which can be arbitrary, but for convenience are chosen to coincide with symmetry elements within the crystal. The repeat distances, a along x , b along y , and c along z , and the angles between the axes, α between y and z , β between x and z , and γ between x and y , define a parallelepiped which is the repeating unit in space and is termed the unit cell. Each unit cell contains the same number of molecules arranged in the same way.

The dimensions of the unit cells of most crystals are of the same order of magnitude as the wavelength of X-rays and therefore crystals can act as three dimensional diffraction gratings for X-rays.

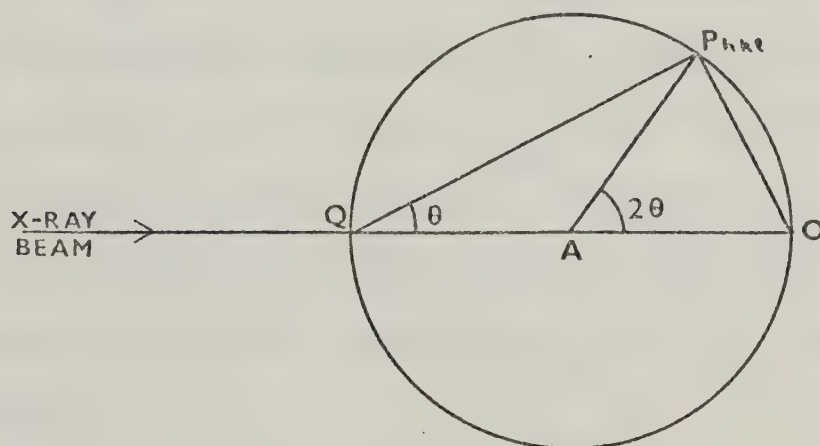
The Reciprocal Lattice

Interaction of X-rays with crystals is accounted for by Bragg's Law, $n\lambda = 2d \sin \theta$, in which sets of parallel planes in the crystal, separated by a distance d , reflect X-rays of wavelength λ when their angle to the beam satisfies the expression. Therefore the specification and identification of the planes is important in interpreting the X-ray diffraction process.

The planes are usually described by the indices

hkl which are the reciprocals of the intercepts of the planes on the unit cell axes. Indexing of the diffraction pattern in terms of these indices is readily done when the planes are considered in terms of a reciprocal space lattice.

The reciprocal lattice may be constructed from the direct lattice by taking a lattice point as origin and constructing normals to all possible direct lattice planes. These normals are terminated a distance $1/d_{hkl} = d_{hkl}^*$ from the origin, where d_{hkl} is the spacing between the sets of planes (hkl) . In this way a set of points, each labelled according to the (hkl) family of planes it represents, are produced, and these constitute the reciprocal lattice. An important property of the reciprocal lattice is that if a sphere is constructed of radius $1/\lambda$, with the reciprocal lattice origin O on its circumference, then every time a reciprocal lattice point hkl coincides with the sphere, then



the real set of planes, parallel to PQ , are in the correct orientation to satisfy the condition for Bragg reflection.

Scattering of X-rays by Matter

An electron located in the path of an X-ray beam will be forced into oscillation by the electromagnetic field of the X-ray impinging upon it and so becomes a source of radiation itself. In this way the electron is said to scatter the X-rays.

The scattering from an atom then will be directly related to the number of electrons it possesses. The efficiency of scattering in a particular direction is known as its atomic scattering factor, f_0 , and is expressed by the ratio $f_0 = A_A/A_e$, where A_A is the amplitude of the wave from the whole atom and A_e the amplitude from a free electron, scattering under the same conditions. Some of the factors which affect f_0 will be discussed later.

The amplitude of a wave in a given direction, scattered by N atoms, is the sum of the scattering power of each of the atoms for that particular diffraction angle. If the phase of the j th atom with respect to the origin is δ_j then the amplitude can be written as $F_\theta = \sum_{j=1}^N f_j e^{i\delta_j}$, where f_j is the scattering factor of the j th atom. The phase δ can be obtained from the positions of the atoms in the unit cell. If the coordinates of the j th atom are x_j, y_j, z_j , then δ_j will be given by:

$$\delta_j = 2\pi(hx_j + ky_j + lz_j). \quad (1)$$

so that the structure factor for a wave diffracted from the

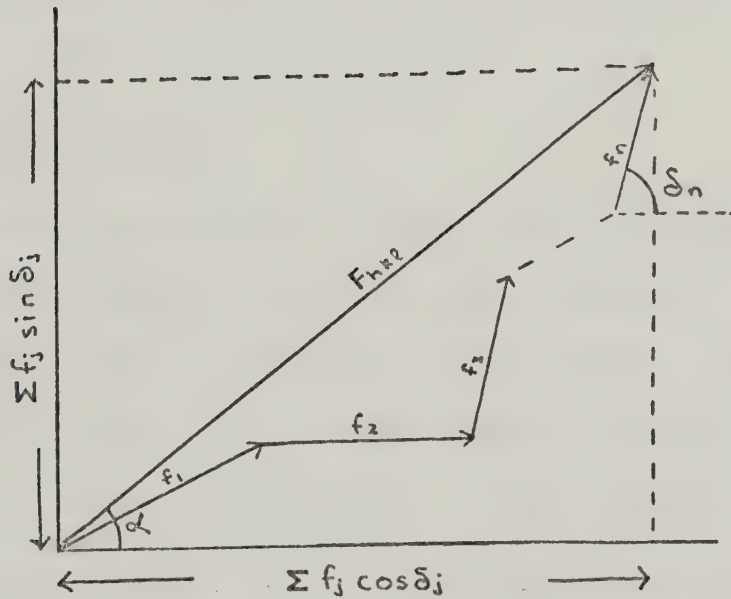
set of planes (hkl) is

$$F_{hkl} = \sum_{j=1}^N f_j \exp [2\pi i(hx_j + ky_j + lz_j)] \quad (2)$$

This can be rewritten as:

$$F_{hkl} = \sum_{j=1}^N f_j \cos 2\pi(hx_j + ky_j + lz_j) + \sum_{j=1}^N f_j i \sin 2\pi(hx_j + ky_j + lz_j) \quad (3)$$

which can be represented in diagrammatic form on the Argand diagram.



From this we see that:

$$|F_{hkl}| = \sqrt{(\sum_j f_j \cos \delta_j)^2 + (\sum_j f_j \sin \delta_j)^2} \quad (4)$$

and
$$\alpha = \tan^{-1} \left(\frac{\sum_j f_j \cos \delta_j}{\sum_j f_j \sin \delta_j} \right) \quad (5)$$

or
$$|F_{hkl}| = \sqrt{A_{hkl}^2 + B_{hkl}^2} \quad \text{and} \quad \alpha = \tan^{-1} \left(\frac{B_{hkl}}{A_{hkl}} \right)$$

With the above formulas structure factor amplitudes and phases can be calculated once the positions of the atoms are known. The expression for the structure factor is a general expression which is modified by the presence of symmetry elements. For example the presence of a centre of symmetry reduces it to

$$F_{hkl} = 2 \sum_{j=1}^{N/2} f_j \cos 2\pi(hx_j + ky_j + lz_j) \quad (6)$$

The Scattering Factor

The scattering factor used in the above calculations has been defined as the scattering power of the atom relative to the scattering power of one electron. The maximum value it can attain then, is Z , the atomic number of the atom and this occurs in the direction of the incident beam, i.e. at $\theta = 0$, since in this direction all the electrons will be scattering in phase. However because of the finite size of the atom, as $\sin \theta / \lambda$ increases, the scattering factor decreases, since the X-rays scattered from an electron in one part of the atom will be, to an increasing extent, out of phase with

those in other parts of the atom, the resulting interference reducing the scattering efficiency.

The scattering power is also subject to thermal effects, since, in general, the higher the temperature, the greater the vibration of the atom. The effect of the vibration or thermal motion is to cause the electrons to sweep out a larger volume than they would occupy if the atom were at rest, thus causing the scattering power to fall off even more rapidly with increasing $\sin \theta/\lambda$. These effects are illustrated in fig. 1.

It has been shown that the required correction to the scattering factor for isotropic vibration is given by:

$$f = f_0 \exp (-B \sin^2 \theta / \lambda^2) \quad (7)$$

where B, known as the isotropic temperature factor, is related to the mean square amplitude of vibration.

When anisotropic vibration is being considered, the exponential term in (7) takes the form $\exp(-h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})$, which describes the magnitude and orientation of a vibrational ellipsoid with respect to the crystallographic axes.

The scattering factor has also to be corrected for the effect of anomalous dispersion, which arises when the wavelength of the incident beam lies near an absorption edge of any of the atomic species present in the crystal. Under

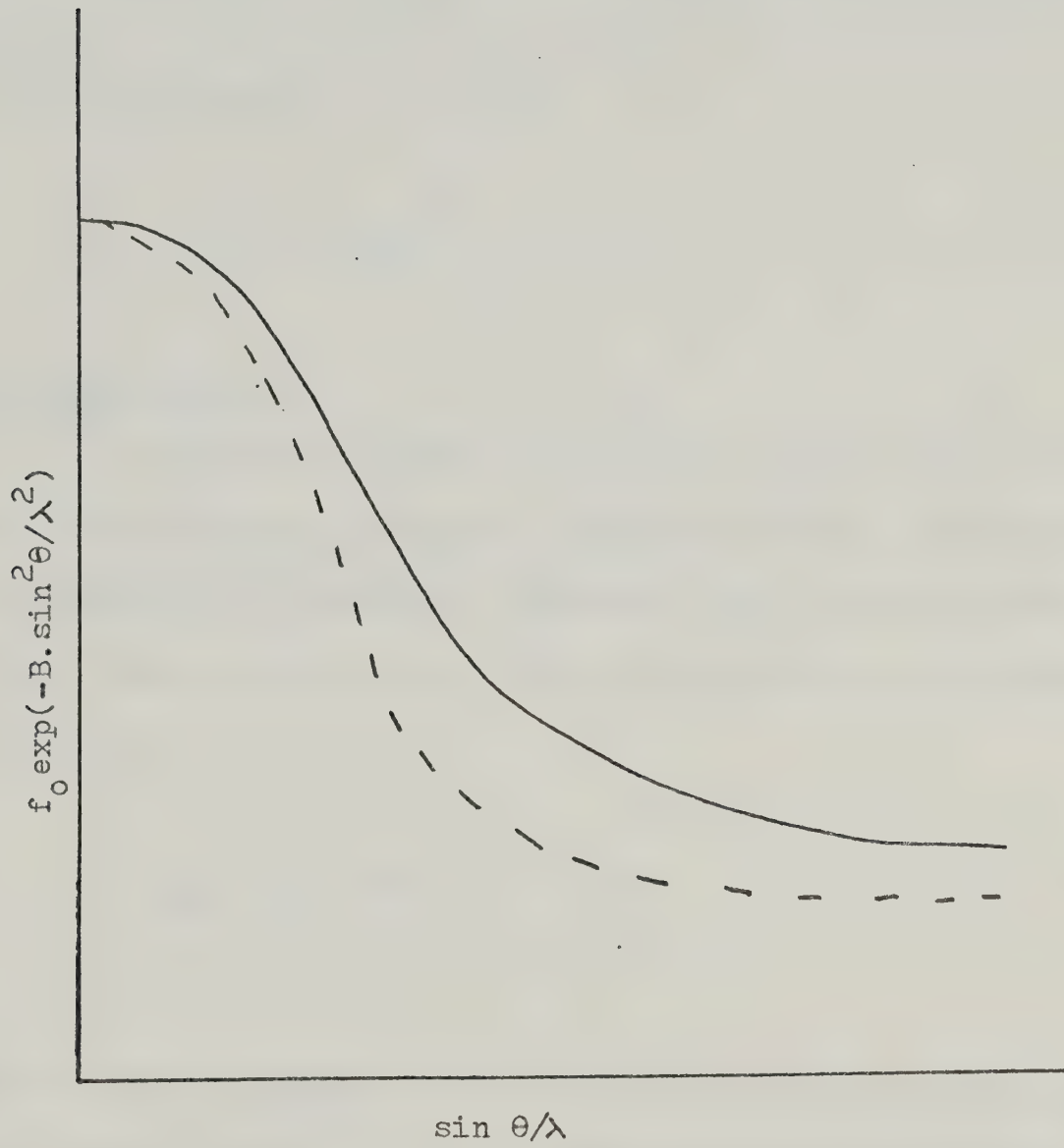


Fig. 1. The variation of f_0 with $\sin \theta / \lambda$ -- no temperature correction ---- $B = 4.0$ applied.

these circumstances, the wave scattered by an atom undergoes an anomalous phase shift. The resultant scattering factor can be expressed by addition of two correction terms, one real and one imaginary, to the normal scattering factor.

$$\begin{aligned} f &= f_0 + \Delta f' + i\Delta f'' \\ &= f' + i\Delta f'' \end{aligned} \tag{8}$$

Data Reduction

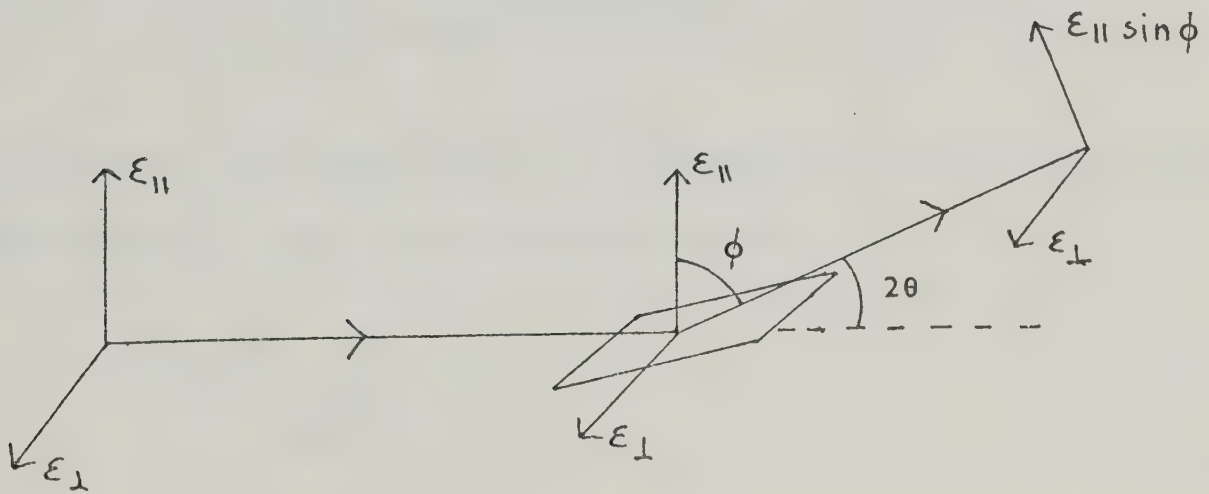
Structure factor amplitudes may be obtained from the experimentally observed intensities after correction has been made for several geometric and physical factors which affect these intensities. The relationship is expressed by the equation:

$$F_{hk\ell} = \sqrt{\frac{K I_{hk\ell}}{L_p}} \tag{9}$$

where K is a constant, L is the Lorentz factor and p the polarisation factor. $I_{hk\ell}$ is the measured intensity.

The polarisation factor arises because the incident beam is unpolarised whereas the reflected beam is partially polarised, which has the effect of decreasing the intensity. The electric vectors in the unpolarised beam may all be considered in terms of their components in two directions,

perpendicular and parallel to the plane of the incident and reflected beam. ($\epsilon_{\perp}$ and $\epsilon_{\parallel}$). Since the electric vectors in the unpolarised beam are randomly oriented, these two components will occur with equal frequency and the intensities associated with each are therefore equal. ie. $I_{\perp} = I_{\parallel} = 1/2 I_{\text{incident}}$



Since the intensity is proportional to the square of the electric vector, after reflection, $I_{\perp}' = k\epsilon_{\perp}^2 = I_{\perp}$

$$\text{and } I_{\parallel}' = k\epsilon_{\parallel}^2 \sin^2 \phi = I_{\parallel} \sin^2 \phi$$

$$= I_{\parallel} \cos^2 2\theta$$

$$\therefore I_{\text{reflected}} = I_{\perp} + I_{\parallel} \cos^2 2\theta$$

$$= 1/2 I_{\text{incident}} + 1/2 I_{\text{incident}} \cos^2 2\theta$$

$$= p I_{\text{incident}}$$

$$\text{where } p = 1/2 + 1/2 \cos^2 2\theta \quad (10)$$

The Lorentz factor L arises because the time required for a reciprocal lattice point to pass through the sphere of reflection varies with the direction in which it approaches the sphere. The correction term has been shown to be

$$L = \frac{\sin \theta}{\sin 2\theta \sqrt{\sin^2 \theta - \sin^2 \mu}} \quad (11)$$

for equi-inclination geometry, in which μ is the equi-inclination angle. This however reduces to

$$L = \frac{1}{\sin 2\theta} \quad (12)$$

for diffractometer data collected by the 2θ scan method.

The term K is a scale factor for putting the $|F|$'s on an absolute scale. Usually scaling is done at a later stage of the analysis.

Other physical effects upon the intensity are primary extinction, secondary extinction and absorption. Primary extinction is an interference process, caused by multiple reflection at a set of planes, which reduces the intensity of the beam as it passes through the crystal. This problem is not important, except in crystals which contain little or no mosaic character where the effect is to make I

$\propto F_{hk\ell}$ rather than $F_{hk\ell}^2$.

Secondary extinction is a more serious problem, which arises when an appreciable amount of the incident radiation is reflected at a given instant by the first planes it encounters, so that deeper planes receive less incident intensity and therefore reflect with reduced power. This effect can be corrected for by a method proposed by Zacharisen which is described later in the thesis.

The effect of absorption is to attenuate the X-ray beam as it passes through the crystal. The effect can be corrected for if the precise geometry of the crystal is known, since then, the exact path length can be determined for a beam reflecting from each infinitesimal portion of the crystal. Integration over the entire volume of the crystal gives the correction factor¹

$$A = \int \frac{1}{V} \exp [-\mu(\ell_1 + \ell_2)] dV \quad (13)$$

where V is the volume of the crystal, μ is the linear absorption coefficient and ℓ_1 and ℓ_2 are the path lengths along the direction of the primary and diffracted beam directions.

When the intensities have been corrected for these effects, structure amplitudes may be determined. The object of the crystal structure analysis then becomes one of finding the structural model which gives the closest agreement between the observed and calculated structure amplitudes.

The Phase Problem

Since a crystal is periodic, its electron density distribution can be represented by a Fourier series

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_\ell F_{hkl} \exp[-2\pi i(hx + ky + \ell z)] \quad (14)$$

or

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_\ell |F_{hkl}| \exp[-2\pi i(hx + ky + \ell z - \alpha_{hkl})] \quad (15)$$

V is the volume of the unit cell, $|F_{hkl}|$ is the structure factor amplitude and $2\pi\alpha_{hkl}$ is its phase. From the measured intensity data, the structure factor amplitudes can be obtained, but the phases cannot. The solution of the crystal structure then, reduces essentially to determining the phases of the structure amplitudes, since when these are known, the electron density within the unit cell can be determined from (15).

The problem of determining the phases is simplified to some extent, in that it is not necessary to arrive at a solution for all the reflections at the outset of the analysis, but only for a large enough number of the stronger intensities to provide an approximation to the structure, which can then be used for calculating the phases of the remaining reflections.

Several methods have been used to obtain a solution

to the phase problem. The two that were used in this thesis will now be described.

The Patterson Method

The electron density in a unit cell may be represented by equation (14). The relationship between that and the function

$$P(u,v,w) = \frac{1}{V^2} \sum_h \sum_k \sum_\ell |F_{hkl}|^2 \exp[-2\pi i(hu + kv + \ell w)] \quad (16)$$

was demonstrated by A.L. Patterson^{2,3}. If $\rho(x,y,z)$ has peaks corresponding to atomic locations in the unit cell, then, $P(u,v,w)$ will have peaks corresponding to the ends of vectors between all pairs of atoms in $\rho(x,y,z)$, radiating from the origin.

This is most easily seen for the one dimensional case. Consider the electron density at the points x and $x + u$ along a line of period a ,

$$\rho(x) = \frac{1}{a} \sum_h F_h \exp(-2\pi i h x)$$

$$\rho(x + u) = \frac{1}{a} \sum_h F_h \exp[-2\pi i h (x + u)]$$

The product of these is:

$$\rho(x)\rho(x + u) = \left(\frac{1}{a} \sum_h F_h \exp(-2\pi i h x) \right) \left(\frac{1}{a} \sum_h F_h \exp[-2\pi i h (x + u)] \right)$$

This is the product of the electron densities at a chosen separation u for a location x which may take all values from 0 to 1. If we work in absolute coordinates, then this is a separation U ($= ua$) for a location X ($= xa$) which may vary from 0 to a . The average value of this product when we allow X to assume all values within the period is given by the integral

$$\begin{aligned}
 A(U) &= \frac{1}{a} \int_0^a \rho(X) \rho(X + U) dX \\
 &= \frac{1}{a} \int_0^a \left(\frac{1}{a} \sum_h F_h \exp(-2\pi i h X / a) \right) \left(\frac{1}{a} \sum_h F_h \exp \right. \\
 &\quad \left. [-2\pi i h (X + U) / a] \right) dX \\
 &= \frac{1}{a} \sum_h \sum_h \int_0^a \left(\frac{1}{a} F_h \exp(-2\pi i h X / a) \right) \left(\frac{1}{a} F_h \exp \right. \\
 &\quad \left. [-2\pi i h (X + U) / a] \right) dX
 \end{aligned}$$

This is the sum of integrals of terms which are products of F_h with F_h , the value of h in the two F 's being, in general, different, and for clarity can be written as m and q . Using this notation and taking terms which do not involve X outside the integral, the equation can be rewritten as

$$\begin{aligned}
A(U) &= \frac{1}{a} \sum_m \sum_q \frac{1}{a^2} F_m F_q \exp(-2\pi i q U/a) \\
&\quad \int_0^a \exp(-2\pi i m X/q) \exp(-2\pi i q X/a) dX \\
&= \frac{1}{a} \sum_m \sum_q \frac{1}{a^2} F_m F_q \exp(-2\pi i q U/a) \\
&\quad \int_0^a \exp[-2\pi i (m + q) X/a] dX
\end{aligned}$$

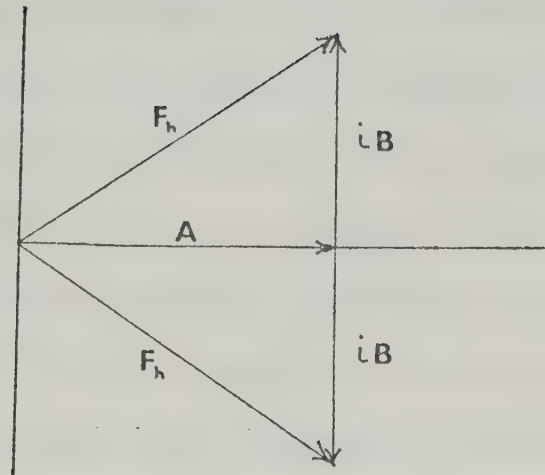
This integral vanishes for all values of m and q except when $q = -m$ in which case it simply reduces to:

$$\begin{aligned}
A(U) &= \frac{1}{a} \sum_m \sum_{-m} \frac{1}{a^2} F_m F_{-m} \exp(-2\pi i m U/a) \int_0^a e^0 dX \\
&= \frac{1}{a} \sum_m \sum_{-m} \frac{1}{a} F_m F_{-m} \exp(-2\pi i m U/a)
\end{aligned}$$

The double summation depends only on m and so can be written as a single summation

$$A(U) = \frac{1}{a^2} \sum_h F_h F_{-h} \exp(-2\pi i h U/a)$$

According to Friedel's Law F_h and F_{-h} have identical magnitudes but opposite phases.



$$\begin{aligned}
 F_h F_{-h} &= (A + iB)(A - iB) = A^2 + B^2 \\
 &= |F_h|^2
 \end{aligned}$$

Substituting this in the equation, we obtain,

$$A(U) = \frac{1}{a} \sum_h |F_h|^2 \exp(2\pi i h U/a) \quad (17)$$

The function will have large values if somewhere in the period a , there are large values of electron density separated by the selected distance u .

Extending this to three dimensions, a peak at (u, v, w) in the Patterson function is related to the peaks of the a th and b th atoms in the electron density function by $u = x_a - x_b$, $v = y_a - y_b$, $z = z_a - z_b$. If there are n atoms in $\rho(x, y, z)$ then there will be n^2 peaks in the Patterson

function, n of which occur at the origin.

When n is small, it is often possible to deduce the correct atomic arrangement from the distribution of peaks in $P(u,v,w)$, especially if the structure or some part of it is known in advance in broad detail. However as the complexity of the molecule increases so does that of its vector pattern. This together with the increased possibility of overlapping peaks can make the interpretation of a Patterson map a difficult task.

To make the identification of single atom-single atom interactions easier, the so called Harker sections may be used. Harker showed that certain sections or lines of the Patterson contained vectors related only by certain of the space group elements⁴. For example if the space group contains a two-fold axis, coincident with the b axis, then if there is an atom at (x,y,z) there will be a crystallographically equivalent atom at $(\bar{x}, y, \bar{z})$. The vector between these atoms has the components $(2x, 0, 2z)$ and consequently there will be a maximum in $P(u,v,w)$ at the point $(2x, 0, 2z)$. There will be such a maximum in the plane $y = 0$ for each different kind of atom in the crystal, and the x and z coordinates for all the atoms in the crystal can consequently be found by evaluating $P(u,v,w)$ for $y = 0$ only. Harker summarized the forms of $P(u,v,w)$ best suited to the various symmetry elements in the manner shown in Table 1.

The problem is further simplified if the molecule

TABLE 1

Forms of $P(x,y,z)$ best suited to the determination of atomic coordinates in crystals having various symmetry elements.

Symmetry Element	Form of $P(x,y,z)$
(a) Axes parallel to b axis	
(i) $2, 4, 4_2, \bar{4}, 6, 6_2, 3, \bar{3}, 6_3$	$P(x, 0, z)$
(ii) $2_1, 4_1, 4_3, 6_1, 6_5$	$P(x, 1/2, z)$
(iii) $3_1, 6_2, 6_4$	$P(x, 1/3, z)$
(b) Planes perpendicular to b-axis	
(i) reflection plane m	$P(0, y, 0)$
(ii) glide plane, glide = $1/2$ a	$P(1/2, y, 0)$
(iii) glide plane, glide = $1/2$ c	$P(0, y, 1/2)$
(iv) glide plane, glide = $1/2$ (a + c)	$P(1/2, y, 1/2)$
(v) glide plane, glide = $1/4$ (a + c)	$P(1/4, y, 1/4)$

contains at least one atom which is substantially heavier than the others. The height of a Patterson peak is directly proportional to the products of the atomic numbers of the atoms between which a vector occurs. Therefore vectors between heavy atoms stand out strongly against the background of heavy-light and light-light atom vectors, and the coordinates of the heavy atoms can therefore be found very often without too much difficulty. The significance of this is that the X-ray scattering will be largely dominated by the heavy atoms and so the approximation may be made that the phases of the structure amplitudes are those which would be required for the heavy atoms alone. The coordinates of the heavy atoms may be used to calculate structure factors and phases and the calculated phases are then combined with the observed structure amplitudes in a Fourier synthesis, which should give an approximation to the electron density distribution in the cell. From this the positions of the lighter atoms may be obtained which can be added to the structure factor and phase calculations and the process repeated until all atom positions are known.

Direct Methods of Phase Determination

In discussing direct methods of phase determination, various forms of the structure factor other than F_{hkl} will be used and are best defined at the outset. The unitary

structure factor $U_{hk\ell}$ is given by

$$U_{hk\ell} = \frac{F_{hk\ell}}{N \sum_{j=1} f_j} \quad (18)$$

where N is the number of atoms in the unit cell. This is a factor with the same phase as $F_{hk\ell}$, but whose values range from -1 to $+1$. As N increases, the average value of $|U|$ decreases, and since the inequality and probability relationships to be discussed later require large $|U|$'s, their use is somewhat limited.

A much more useful term is the normalised structure factor $E_{hk\ell}$ given by:

$$E_{hk\ell}^2 = \frac{U_{hk\ell}^2}{\bar{U}^2} \quad (19)$$

or

$$E_{hk\ell}^2 = \frac{|F_{hk\ell}|^2}{\epsilon \sum_{j=1}^N f_j^2} \quad (20)$$

where ϵ is an integer which corrects for space group extinctions. The advantage of using $E_{hk\ell}$'s is that the average value of $E_{hk\ell}^2$ is always 1 and is therefore independent of the complexity of the structure.

The origin of direct methods can probably be traced back to the work of Harker and Kasper on inequality relation-

ships⁵. By application of the classical Schwarz and Cauchy inequalities to the structure factor expressions, they were able to derive the seemingly trivial result:

$$|F_{hk\ell}|^2 \leq F_{000}^2 \quad \text{or} \quad |U_{hk\ell}|^2 \leq 1$$

However on addition of the requirement of centrosymmetry, decidedly non-trivial results were obtained, e.g.

$$U_{hk\ell}^2 \leq 1/2(1 + U_{2h,2k,2\ell})$$

which, if both U's are large, would require that $U_{2h,2k,2\ell}$ be positive for the inequality to hold. Other inequality relationships can be derived for this symmetry element and for the addition of other symmetry requirements.

Sayre used the self convolution theorem to arrive at an equation interrelating structure factors for crystals containing equal resolved atoms⁶. The self convolution theorem states that if a function is represented as a Fourier series, then the coefficients of the Fourier series of the squared function may be found from:

$$F_{(hk\ell)}^{sq} = \frac{1}{V} \sum_p \sum_q \sum_r F(pqr) F(h-p, k-q, \ell-r) \quad \text{for all } hk\ell.$$

The $F_{hk\ell}$ and the $F_{hk\ell}^{sq}$ are related to each other by a simple scaling term and so the equation can be rewritten as:

$$F_{hkl} = \frac{\theta_{hkl}}{V} \sum_p \sum_q \sum_r F_{pqr} F_{(h-p)(k-q)(l-r)} \quad (19)$$

Thus an array of phases can only be correct if it causes this relationship to be satisfied. Although this relationship is valid whether or not the crystal possesses a centre of symmetry, Sayre only used it for the centrosymmetric case. It would appear from the equation that in order to determine the sign of F_{hkl} it would be necessary to know the magnitude and phases of all others. However, Sayre pointed out that in the centrosymmetric case, if F_{hkl} is large, the series must tend strongly in one direction (+ or -). The products which contribute most to this direction in the summation will be those between large $|F|$ and so for the case of large reflections, we have

$$S(F_{hkl}) \sim \left(S \sum_p \sum_q \sum_r F_{h-p, k-q, l-r} F_{pqr} \right) \quad (20)$$

where S is 'the sign of', and $\sim$ means probably equal to, and the suffix r means that the summation is carried out only for large $|F|$.

This work paralleled the work of Karle and Hauptmann, who using the criterion that the electron density distribution had to be a non-negative function, derived a complete set of inequalities, which are valid for all space groups and embraced the Harker-Kasper inequalities⁷. The inequalities could be written as a series of relationships which increased

in complexity. The first three were:

$$F_{000} \geq 0 \quad (21)$$

$$|F_{hkl}| \leq F_{000} \quad (22)$$

$$\left| F_{(h_1+h_2, k_1+k_2, \ell_1+\ell_2)} - \frac{F_{h_1 k_1 \ell_1} \cdot F_{h_2 k_2 \ell_2}}{F_{000}} \right| \leq \frac{\left| \begin{array}{cc} F_{000} & F_{\bar{h}_1 \bar{k}_1 \bar{\ell}_1} \\ F_{h_1 k_1 \ell_1} & F_{000} \end{array} \right|^{1/2} \left| \begin{array}{cc} F_{000} & F_{\bar{h}_2 \bar{k}_2 \bar{\ell}_2} \\ F_{h_2 k_2 \ell_2} & F_{000} \end{array} \right|^{1/2}}{F_{000}} \quad (23)$$

It is this third inequality which parallels the Sayre relationship. If we let $h = h_1 + h_2$, $k = k_1 + k_2$, $\ell = \ell_1 + \ell_2$ and $k = h_2$, k_2 , ℓ_2 , then (23) can be rewritten.

$$F_h - \frac{F_{h-k} F_k}{F_{000}} \leq \frac{\left| \begin{array}{cc} F_{000} & F_{h-k}^* \\ F_{h-k} & F_{000} \end{array} \right|^{1/2} \left| \begin{array}{cc} F_{000} & F_k^* \\ F_k & F_{000} \end{array} \right|^{1/2}}{F_{000}} \leq r \quad (24)$$

The larger the values of $|F_{h-k}|$ and $|F_k|$ the smaller

will be r and the closer will be F_h to $F_{h-k} F_k / F_{000}$. Since k can be varied arbitrarily there will be many such relationships and it would be expected that F_h would be proportional to the average $F_{h-k} \cdot F_k / F_{000}$, involving the larger $|F|$ s, as k is varied. i.e.

$$F_h \propto \langle F_k \cdot F_{h-k} \rangle_k \quad (25)$$

which gives the same result as the Sayre relationship for centrosymmetric crystals if large structure factor magnitudes are involved.

Since $F_h = |F_h| \exp(i\phi_h)$ then

$$\phi_h \approx \langle \phi_k + \phi_{h-k} \rangle_k \text{ follows from this.}$$

The Sayre relationship (20) can be expressed in terms of normalised structure factors, when it becomes the Σ_2 relationship of Hauptmann and Karle⁸.

$$S(E_h) \sim S(\sum_k E_k E_{h-k}) \quad (26)$$

This relationship is a probability relationship. The probability that the sign of E_h be positive was given by Woolfson⁹ and Woolfson and Cochran¹⁰, which when expressed in terms of normalised structure factors is,

$$P_{+(h)} = \frac{1}{2} + \frac{1}{2} \tanh\left\{\frac{\sigma_3}{\sigma_2^{3/2}} |E_h| \sum_k E_k E_{h-k}\right\} \quad (27)$$

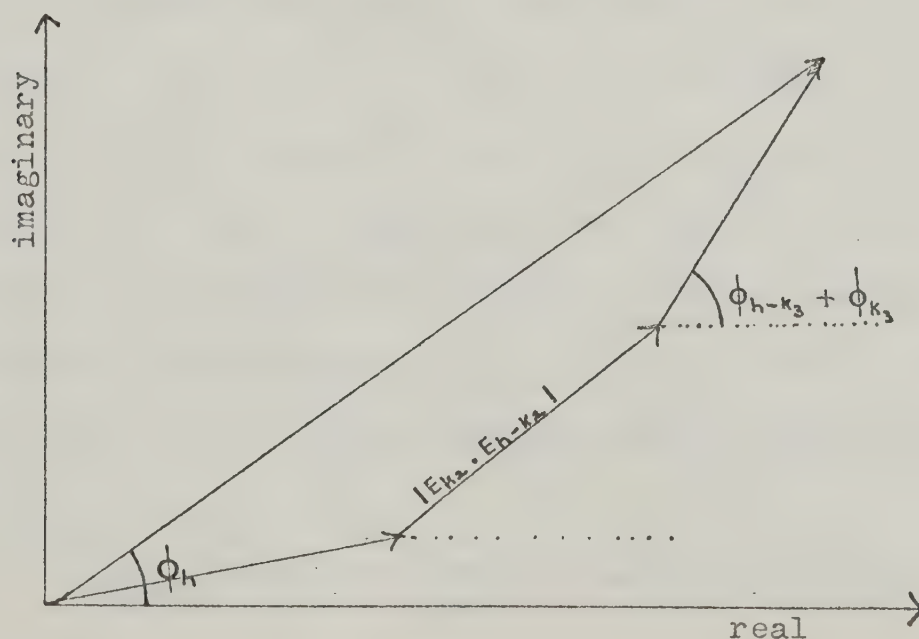
where $\sigma_3 = \sum_i^N n_i^3$, $\sigma_2 = \sum_i^N n_i^2$ and

$$n_i = \frac{f_i}{\sum_{j=1}^N f_j}.$$

The Σ_2 relationship can be used in conjunction with this probability formula to give a set of phases, for centrosymmetric space groups, which have a high probability of being correct.

For non centrosymmetric cases, the sum of the angles formula $\phi_h \approx \langle \phi_{h-k} + \phi_k \rangle_k$ may be used but it presents difficulties when the phase indications are very different.

It has been found better, to regard each phase indication as a vector of length $|E_{h-k} \cdot E_k|$ and direction $(\phi_{h-k} + \phi_k)$ and to add them vectorially.



From this we obtain

$$\tan \phi_h = \frac{\sum_k |E_k E_{h-k}| \sin(\phi_k + \phi_{h-k})}{\sum_k |E_k E_{h-k}| \cos(\phi_k + \phi_{h-k})} \quad (28)$$

which is the tangent formula of Karle and Hauptmann¹¹.

The Σ_2 relationship for centrosymmetric crystals and the sum of the angles and tangent formulas for non-centrosymmetric crystals all need a basic set of phases in order to use them for obtaining additional phases. The Karles have generalised the procedure for obtaining the basic set and extending them in both the centrosymmetric and non-centrosymmetric cases, using what they have termed 'the symbolic addition procedure'¹².

The basic set used is composed of those phases necessary to fix the origin and some additional phases denoted by symbols corresponding to the large $|E|$.

Three or less phases, depending on the space group, may be assigned arbitrarily, subject to certain restrictions, to specify the origin⁸. Consider the space group $P\bar{1}$. Here there are eight possible centres which could be used as the origin of the cell. Changing the origin affects the phases of many of the structure factors. For a structure of N atoms with coordinates x_j, y_j, z_j , etc., with respect to the origin $(0,0,0)$ the structure factor expression is

$$F_{hkl}(0,0,0) = \sum_{j=1}^N f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

Changing the origin to the point $(1/2, 0, 0)$ say, the equation becomes

$$F_{hk\ell}(1/2, 0, 0) = \sum_{j=1}^N f_j \cos 2\pi (h(x_j + 1/2) + ky_j + \ell z_j) \\ = (-1)^h F_{hk\ell}(0, 0, 0)$$

which is $+ F_{hk\ell}(0, 0, 0)$ for h even (e) or $-F_{hk\ell}$ for h odd (o). By considering the other alternative origins in the same way, it is found that the structure factors may be divided into eight groups that behave differently, according to the parities of h, k and ℓ . This is summarized in Table 2, for the eight possible origins.

Reflections for which h, k and ℓ are all even (eee) are unaffected by the origin shifts. These are known as structure invariants. They are determined solely by the structure and are independent of the origin choice, and therefore can not be given values at will. All other classes are positive for four origins and negative for the other four. One member from one of these sets may be assigned a phase arbitrarily since this merely corresponds to selecting one origin set (+ or -) from the two possibilities, reducing the possible number of origins to four. The phases of all the reflections of this class are now fixed and no further choices

TABLE 2

Variation of Structure Factor Sign with Origin and Parity
of the Reflection

	Origin	eee	eeo	oeo	ooo	oeo	oeo	ooo	ooo
1.	0,0,0	+	+	+	+	+	+	+	+
2.	0,0,1/2	+	-	+	-	+	-	+	-
3.	0,1/2,0	+	+	-	-	+	+	-	-
4.	0,1/2,1/2	+	-	-	+	+	-	-	+
5.	1/2,0,0	+	+	+	+	-	-	-	-
6.	1/2,0,1/2	+	-	+	-	-	+	-	+
7.	1/2,1/2,0	+	+	-	-	-	-	+	+
8.	1/2,1/2,1/2	+	-	-	+	-	+	+	-

can be made from this set. All the remaining classes however (except eee) are positive for two of these origins and negative for the other two. Thus a reflection from one of these classes can be assigned a phase, which reduces the choice of origin to two possibilities. A third reflection can now be chosen from another class and assigned a phase and this will assign the origin uniquely. However there are restrictions on this choice, in that it must be linearly independent of the other two, i.e. the parity sum of the three classes must not equal eee. For example, if a reflection from the parity group (eeo) had been assigned a phase of +, inspection of Table 2 shows that the origin choices has been restricted to origins 1,3,5 and 7. Now assigning a phase of + to a reflection from the parity group (eoe), further restricts the origin choice to 1 or 5. Now the assignment of a third phase is restricted to a reflection from one of the parity groups oee, oeo, ooe or ooo, since if eoo is taken the parity sum of eeo + eoe + eoo = eee, which is not allowed.

The above applies to all primitive space groups for the classes triclinic through orthorhombic. Addition of centring merely places a restriction on the origin, e.g. in the space group $C_{2/c}$ there are only four possible origin centres. Therefore only two reflections need be assigned phases to fix the origin, but these must be chosen from a class for which l is odd.

For the non-centrosymmetric case a further phase

must be assigned to fix the enantiomorph¹³. This is assigned to an invariant and it must not be 0 or π .

Along with the origin-defining phases, other reflections with large $|E|$ are given symbols as phases. These are used in the Σ_2 or tangent formula to produce a set of phases in terms of these symbols. Usually relationships between the symbols appear during the process, so that at the end of the phase determining procedure you may be left with only a few symbolic signs unknown. In any case relatively few E maps (Fourier maps in which the E_{hkl} are the coefficients) need be produced, from which if the phasing has been successful a chemically reasonable structure or part of a structure can be found.

If only part of the structure is found it can be used to produce a Fourier from which the positions of other atoms may be found, as described at the end of the section dealing with the Patterson method. Another powerful tool in the location of missing atoms in the model is the difference Fourier. This is a Fourier in which ΔF 's ($= |F_o| - |F_c|$) are used as coefficients. Obviously this will be sensitive to errors in the model and so, if the model is incomplete, peaks will appear in positions where there are missing atoms.

Least Squares Refinement

The positions of the atoms in the unit cell obtained by the above methods give a rather crude model. In order to determine the accurate structure it is necessary to

refine the atom parameters. A powerful method for doing this involves the principle of least squares. The principle of least squares says that, for a linear function with n variables $(x_1, x_2, \dots, x_n)$, whose value is determined by these variables and a set of independent parameters $p_1, \dots, p_n$, such that:

$$f = p_1 x_1 + p_2 x_2 + \dots + p_n x_n, \quad (29)$$

then, if the value of the function is measured at m different points, the best values for the parameters $p_1, \dots, p_n$ are those which minimise the sums of the squares of the properly weighted differences between the observed and calculated values of the function for all m points. Thus the quantity to be minimised is given by:

$$D = \sum_{r=1}^m W_r (f_{o_r} - f_{c_r})^2 \quad (30)$$

In order for this function to be a minimum, the derivative of the right hand side must be zero. That is,

$$\sum_{r=1}^m W_r (f_{o_r} - f_{c_r}) \frac{\partial f_{c_r}}{\partial p_j} = 0 \quad (j = 1, 2, \dots, n) \quad (31)$$

Substituting for f_{c_r} and $\partial f_{c_r} / \partial p_j$, we obtain n equations known as the normal equations.

$$\sum_{r=1}^m W_r (f_{o_r} - x_{r1} p_1 - x_{r2} p_2 - \dots - x_{rn} p_n) x_{r1} = 0$$

$$\begin{array}{l} \sum_{r=1}^m W_r (f_{o_r} - x_{r1} p_1 - x_{r2} p_2 - \dots - x_{rn} p_n) x_{r2} = 0 \\ \vdots \\ \sum_{r=1}^m W_r (f_{o_r} - x_{r1} p_1 - x_{r2} p_2 - \dots - x_{rn} p_n) x_{rn} = 0 \end{array}$$

which on rearranging gives,

$$\sum_{r=1}^m W_r x_{r1}^2 p_1 + \sum_{r=1}^m W_r x_{r1} x_{r2} p_2 + \dots + \sum_{r=1}^m W_r x_{r1} x_{rn} p_n =$$

$$\sum_{r=1}^m W_r f_{o_r} x_{r1}$$

$$\sum_{r=1}^m W_r x_{r2} x_{r1} p_1 + \sum_{r=1}^m W_r x_{r2}^2 p_2 + \dots + \sum_{r=1}^m W_r x_{r2} x_{rn} p_n =$$

$$\begin{array}{l} \vdots \\ \sum_{r=1}^m W_r f_{o_r} x_{r2} \\ \vdots \end{array}$$

$$\sum_{r=1}^m W_r x_{rn} x_{r1} p_1 + \sum_{r=1}^m W_r x_{rn} x_{r2} p_2 + \dots + \sum_{r=1}^m W_r x_{rn}^2 p_n =$$

$$\sum_{r=1}^m W_r f_{o_r} x_{rn}$$

from which the best values of the p's may be obtained.

If the function is nonlinear, then it can be approximated as a Taylor series

$$f(p_1 p_2 \dots p_n) = f(a_1 a_2 \dots a_n) + \frac{\partial f(a_1 a_2 \dots a_n) (p_1 - a_1)}{\partial p_1} + \dots + \frac{\partial f(a_1 a_2 \dots a_n) (p_n - a_n)}{\partial p_n} \quad (32)$$

in which the $a_1 \dots a_n$ are approximations of the $p_1 \dots p_n$. If $(p_1 - a_1)$ to $(p_n - a_n)$ are given the symbols $\Delta p_1 \dots \Delta p_n$, then if the a_j are a good approximation, the a'_j given by

$$a'_j = a_j + \Delta p_j$$

will be a closer approximation to p_j . The process is iterative and eventually converges at the best values for the various p 's.

In a crystallographic least squares refinement, the function being minimised is

$$D = \sum_{hkl} W_{hkl} (|F_o| - |kF_c|)^2 \quad (33)$$

The weighting function W_{hkl} can be obtained from the standard deviation of the $|F_o|$ since,

$$W_{hkl} = \frac{1}{\sigma_{hkl}^2} \quad \text{and} \quad \sigma_{hkl} = \frac{k}{\sqrt{Lp}} \cdot \frac{\sqrt{\sigma}}{2|F_o|}$$

σ is defined on page 42

The scale factor is applied to Fc since if it is applied to Fo the least squares process minimises D by reducing $|kFo|$ and $|Fc|$ to zero. This it does by reducing k to zero to remove $|kFo|$ and by increasing the thermal parameters to reduce $|Fc|$.

Taking the derivative of the right hand side of (33) and setting it to zero we obtain

$$\sum_{hkl} W_{hkl} (|Fo| - |kFc|) \frac{\partial |kFc|}{\partial p_j} = 0 \quad j = 1, 2, \dots, n \quad (34)$$

Substituting for kFc and $\partial kFc / \partial p_j$ with Fc in the form of a Taylor series we obtain the n normal equations:

$$\begin{aligned} & \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_1}^2 \Delta p_1 + \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_1} \frac{\partial |kFc|}{\partial p_2} \Delta p_2 + \\ & \dots + \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_1} \frac{\partial |kFc|}{\partial p_n} \Delta p_n = \sum_{hkl} W_{hkl} \Delta F \frac{\partial |kFc|}{\partial p_1} \\ & \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_2} \frac{\partial |kFc|}{\partial p_2} \Delta p_1 + \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_2}^2 \Delta p_2 + \dots \\ & \cdot \\ & \cdot \\ & + \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_2} \frac{\partial |kFc|}{\partial p_n} \Delta p_n = \sum_{hkl} W_{hkl} \Delta F \frac{\partial |kFc|}{\partial p_2} \\ & \cdot \\ & \cdot \\ & \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_n} \frac{\partial |kFc|}{\partial p_1} \Delta p_1 + \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_n} \frac{\partial |kFc|}{\partial p_2} \Delta p_2 + \end{aligned}$$

$$\dots + \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_n}^2 \Delta p_n = \sum_{hkl} W_{hkl} \Delta F \frac{\partial |kFc|}{\partial p_n}$$

The various Δp 's can be found from these equations. These, when added to the initial a 's will give a better approximation which can be used in the above process to obtain a still better approximation. The process is repeated until it converges.

The above equations can be written in matrix notation with

$$a_{ij} = \sum_{hkl} W_{hkl} \frac{\partial |kFc|}{\partial p_i} \frac{\partial |kFc|}{\partial p_j}, \quad x_j = \Delta p_j,$$

$$v_i = \sum_{hkl} W_{hkl} F \frac{\partial |kFc|}{\partial p_i}$$

$$\begin{pmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} = \begin{pmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{pmatrix}$$

or

$$Ax = v \text{ so that } x = A^{-1}v.$$

If the elements of A^{-1} are b_{ij} , then, the standard deviations of the variables are given by

$$\sigma_{p_j} = \sqrt{b_{jj} (\sum W_{hkl} \Delta F^2) / (m-n)}$$

where m is the total number of observations and should exceed n .

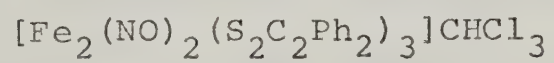
For a more detailed treatment of the material in this chapter, the reader is referred to the following texts:

G.H. Stout and L.H. Jensen, 'X-Ray Structure Determination', MacMillan Co., New York, 1968.

M.J. Buerger, 'Crystal Structure Analysis', Wiley and Sons Ltd., New York, 1967.

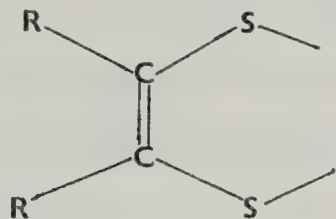
CHAPTER ONE

The Crystal and Molecular Structures of



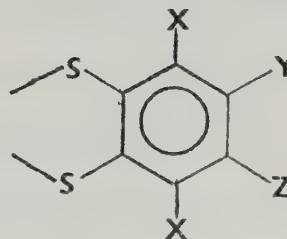
INTRODUCTION

Transition metal complexes containing the 1,2-dithiolene ligands (1 and 2)



1

R = H, CH₃, CF₃, CN, C₆H₅



2

X = Y = Z = H, CH₃, F, Cl

X = Y = H, Z = CH₃

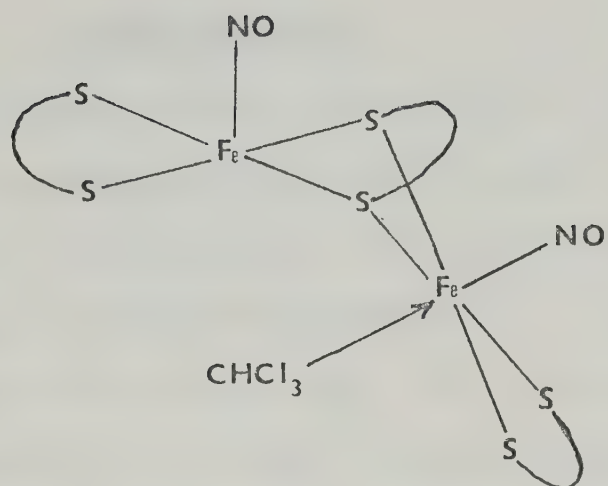
X = H, Y = Z = CH₃

have been extensively studied over the last decade,^{14,15} since the almost simultaneous appearance in 1962 of two short communications^{16,17} concerning the synthesis of the neutral and dianionic bisdithiolene complexes of nickel [Ni{S₂C₂(CN)₂]₂^{0,-2}. The interest in these compounds arose primarily from the chemical and structural properties of the "pure" dithiolene complexes. The bis complexes have been found to possess square planar geometry for a large range of metals¹⁸⁻²⁶, and for any given metal and ligand the complex is capable of stable existence in more than one oxidation state. These are often readily interconverted by reversible one-electron transfer reactions²⁷. These ligands have also been found to stabilise the unusual trigonal prismatic geometry in the neutral tris complexes²⁸⁻³². Again these compounds undergo facile one-electron transfer reactions^{33,34} although

it would appear that the reduced complexes are no longer trigonal prismatic but distorted towards octahedral coordination^{15,35}.

In their investigations into the synthesis and characterisation of these and related complexes, McCleverty and co-workers isolated the complexes $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)_3]^{0,-1}$ which were found to possess several interesting properties³⁶⁻³⁸. The neutral complex displayed two terminal nitrosyl stretching frequencies in the solid state and in solution. The Mössbauer spectrum revealed the presence of two distinct iron sites^{39,40}. The monoanion exhibited an E.S.R. spectrum in solution which consisted of a three line multiplet due to hyperfine interactions with only one ^{14}N whereas a quintet would have been expected if both N's coupled.

From the Mössbauer data, a structure 3 has been tentatively put forward for the neutral complex which involves interaction with the solvent of crystallisation at one of the iron sites⁴⁰. However, it was by no means certain that this was in fact the true structure, and so, in order to unambiguously determine the structure of the molecule and to try to explain some of the properties of both it and the monoanion, a full X-ray crystal structure determination of the neutral complex $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)_3] \cdot \text{CHCl}_3$ was undertaken.



EXPERIMENTAL

Very deep purple, almost black, irregularly shaped crystals of $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)_3]\text{CHCl}_3$ were prepared by McCleverty and co-workers, by the action of nitrous oxide on $[\text{Fe}(\text{S}_2\text{C}_2\text{Ph}_2)_2]_2$ in cold chloroform^{36,37}. Attempts at recrystallisation from chloroform, led to what appeared to be triclinic crystals, but which on subsequent examination by Laue photographs, proved to be powders. Consequently, several small crystals from the irregularly shaped batch were mounted on glass fibres and examined by Laue photographs until one was found which was considered suitable for data collection and photographic work. The dimensions of the crystal were 0.32 mm x 0.14 mm x 0.09 mm.

Weissenberg photographs for the $hk0$, hkl , and $hk2$ layers and precession photographs for the $h0l$ and Ok_l layers were obtained. These showed the Laue symmetry to be mmm and the crystals to be orthorhombic. The following systematic absences:

- (i) $Ok_l \quad k + l = 2n + 1 \quad \text{--} \quad \text{implying an } n \text{ glide perpendicular to } a$
- (ii) $h0_l \quad h + l = 2n + 1 \quad \text{--} \quad \text{implying an } n \text{ glide perpendicular to } b$

defined the space group as either $\text{Pnn}2$ or Pnnm .

The lattice parameters were obtained from the two zero layer precession photographs and the errors in these parameters were calculated by the method of Patterson and Love⁴¹. These results were: $a = 21.82(2)$, $b = 21.20(2)$,

$c = 9.50(1)$. (The figure in parentheses gives the error in the last figure quoted).

The experimental determination of density by flotation in an aqueous solution of potassium iodide gave a range of values from 1.366 to 1.454 gms. cm.⁻³ with an average value of 1.42 gms. cm.⁻³.

The calculated densities for a unit cell of volume 4394.5 Å³ containing four molecules of complex and 0, 0.5, and 1 molecule of chloroform per molecule of complex were 1.358, 1.448, and 1.538 gms. cm.⁻³ respectively. The observed density then corresponded most closely to one half a molecule of CHCl₃ per molecule of complex, but was obviously variable.

The requirement of four molecules of complex in the unit cell places no restrictions on the position of the molecule in the unit cell for the space group Pnn2, but does dictate that the molecule sit either in the mirror plane or on the two-fold axis if the space group is Pnnm, since there are eight general positions in this space group.

Intensity data were collected on a PAILRED automatic diffractometer using graphite crystal monochromated Mo K α radiation and included the layers $hk\ell$ for $\ell = 0$ to 8. Because of the small size of the crystal, the intensities were generally low, and a slow scan rate of 0.25°/min. was used throughout the data collection. The scan width, however, varied, increasing as the layer number increased. For $\ell = 0$

the scan width was 1.8° while for $\ell = 8$ it was 2.2° . A stationary background count for 100 seconds was taken on each side of the scan.

Since the PAILRED diffractometer necessarily gives both the $hk\ell$ and $\bar{h}k\ell$ data, which are equal for the case of either of the two possible space groups, the two data sets were averaged before data reduction.

In the data reduction process, reflections were rejected on the basis of two criteria:

$$(i) \quad I \leq 0$$

$$(ii) \quad I \leq 2\sigma$$

$$\text{where } I = T - tB \text{ and } \sigma = [T + tB + (pI)^2]^{1/2}$$

T is the total integrated peak count obtained in time t_1 , B is the total background count obtained in time t_2 , t is the ratio t_1/t_2 and the p term accounts for machine errors. Of the 2023 reflections measured, 638 were rejected in this way giving 1385 observed reflections.

Measurement of three standard reflections at the end of each layer showed that no significant decomposition took place during the data collection.

Absorption was kept at a minimum by use of $\text{MoK}\alpha$ radiation. Because of this, together with the irregular shape of the crystal, no absorption correction was applied. The linear absorption coefficient for this compound was 10.67 cm.^{-1} .

Corrections for Lorentz and polarisation effects

were applied and structure amplitudes and standard deviations calculated.

At this stage of the study, it was quite clear that the data set would allow the determination of the gross structure, but that any detailed discussion of bond lengths would be precluded.

SOLUTION OF STRUCTURE AND REFINEMENT

A Patterson map was computed, and inspection of the Harker plane at $z = 0$ and the Harker line at $x = 0$, $y = 0$, confirmed the space group as Pnn2. The Harker plane at $z = 0$ contained peaks corresponding to vectors between atoms related by a two-fold axis, these being of the general type $(2x, 2y, 0)$. Both space groups would have given this type of vector. However, if the space group were Pnnm, then additional peaks would have appeared on the Harker line, corresponding to vectors between atoms related by the mirror plane, except for the case where both atoms sit in the mirror plane and have a z coordinate of zero. These vectors have the form $(0, 0, 2z)$.

The three possible situations that could have existed for the space group Pnnm were:

- (i) The molecule sits on the two-fold axis. -- The Harker plane would contain the intramolecular iron-iron vector and the Harker line a peak corresponding to the intermolecular iron-iron vector between the mirror related iron atoms.
- (ii) The molecule sits in the mirror plane and the two iron atoms are mirror related. -- The Harker line would contain the intramolecular iron-iron vector.
- (iii) The molecule sits in the mirror plane, the two iron atoms having $z = 0$ but different x and/or y coordinates. -- No iron-iron vectors would appear on the Harker line, but the Harker plane would contain four peaks corresponding to

an iron-iron intramolecular vector and three iron-iron intermolecular vectors, and these peaks would be arranged in a definite pattern. The iron-iron intramolecular vector would be about $2.5 - 3.5 \text{ \AA}$ from the origin. The other three peaks would be in a straight line which would be parallel to the line between the intramolecular vector and the origin, and would be separated from each other by the intramolecular iron-iron distance.

The Harker line contained only one medium-sized peak $1.67 \text{ \AA}$ from the origin. This clearly eliminated the first two possibilities since this peak was too small and too close to the origin to be either an inter- or an intramolecular iron-iron vector. None of the peaks in the Harker plane conformed to the pattern described in the third possibility. The space group was therefore taken to be $Pnn2$.

Four of the peaks in the Harker plane were interpreted as being due to the two iron-iron intermolecular vectors of the type $(2x, 2y, 0)$ and two iron-sulphur "image vectors", these appearing in the Harker plane, because the plane formed by the two sulphur atoms and the iron to which they were attached, lay parallel to the Harker plane. This S - Fe - S pattern is repeated at the origin as normal intramolecular vectors.

This interpretation gave the x and y coordinates of the two iron atoms and two sulphur atoms, and the z coordinate of the sulphur atoms relative to the iron atom to which they

were attached. With the x and y coordinates of the two iron atoms known, the intramolecular iron-iron vector was easily found and from this, the difference in z coordinate between the two iron atoms was determined. Since there is no unique origin along the two-fold axis of the space group $Pnn2$, the z coordinate of one of the iron atoms was fixed arbitrarily at 0.1 and was not refined. The z coordinates of the other three atoms were determined relative to this atom.

These four atoms positions were used as input to a structure factor calculation, which gave a residual R factor of 0.472. The calculated phases were used to compute an electron density map, which revealed the positions of the other four sulphur atoms.

Two cycles of refinement, using the positions of all eight atoms in the structure factor calculation, reduced the R factor to 0.318 at which point an electron density difference map was computed, from which the positions of all the light atoms in the molecule were found.

In order to reduce the number of variables in the remaining full matrix least squares refinement, and hence computer storage, the phenyl rings were refined as rigid bodies with a C-C distance of $1.397 \text{ \AA}$ and a C-C-C bond angle of 120° .

In four cycles of refinement, with all these atoms included, the R factor fell to 0.153. An electron density difference Fourier gave evidence of anisotropic thermal motion

on the part of the eight heavy atoms. Consequently, these were allowed to refine anisotropically and the R factor reduced to 0.123. Inclusion of the hydrogen rigid bodies on the phenyl rings, in which the C-H distance was 1.0 Å and the temperature factors of the hydrogen atoms were fixed at a value 10% greater than that of the carbon atom to which they were attached, further reduced the R factor to 0.114.

An electron density difference map was calculated and showed no features consistent with an ordered chloroform molecule. Two relatively small peaks ($1.56 \text{ e } \text{\AA}^3$) were located in a pocket between molecules, having a separation of the order found between chlorine atoms in a chloroform molecule. These two were included in the refinement as chlorine atoms and, in accordance with the density experiment, were given half weight. The R factor converged to 0.098. The weighted R factor, defined as $R_2 = [\sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ where w is a weighting factor, was 0.124. An electron density difference map did not yield the positions of the remaining carbon and chlorine atom of the chloroform molecule, the residual density being mainly associated with one of the rigid bodies ($0.94 \text{ electrons/\AA}^3$). This was assumed to be due to the variable occupancy and possible disorder of the molecule and the relatively poor quality of the data.

The scattering factors for all atoms other than hydrogen in the above calculations were calculated from

Cromer's coefficients⁴². The scattering factors for hydrogen were those of Mason and Robertson⁴³.

Since the space group is polar in the z direction, the solution corresponding to the structure of opposite hand was refined. This solution was obtained simply by changing the sign of the z coordinate of each atom. The R factor converged to 0.099 with $R_2 = 0.125$. A Hamilton test⁴⁴ showed that the hypothesis that this solution best described the correct structure could be rejected at the 0.005 confidence level. This statistical test cannot be accepted at face value in view of the poor quality data set. However, the dispersion effects are small in this structure and since only the gross features are to be discussed, an error in choice of handedness is not considered important.

RESULTS

Table 3 gives the observed ($|F_o|$) and calculated ($|F_c|$) structure amplitudes (electrons X 10). The final atomic coordinates for all atoms and isotropic temperature factors for the light atoms are listed in Table 4, the anisotropic temperature factors for iron and sulphur atoms in Table 5. In these tables and all those which appear later, standard deviations in the least significant figures are given in parentheses. Interatomic distances and angles are listed in Tables 6 and 7. Table 11 gives the iron-sulphur distances found in dithiolene complexes while the geometry of the cis-1, 2-diphenyl dithiolene ligand is summarised in Table 12.

A diagram of the whole molecule is shown in Fig. 2. A packing diagram of the contents of the unit cell projected into the [a][b] plane is shown in Fig. 3.

In Table 5 and all other tables of anisotropic temperature factors, the U_{ij} are related to the β_{ij} (page 6) by:

$$U_{ij} = \frac{\beta_{ij}}{2 \pi^2 x_i x_j}$$

where for $i = 1$ $x_i = a^*$

$i = 2$ $x_i = b^*$

$i = 3$ $x_i = c^*$

TABLE 3

Observed and Calculated Structure Amplitudes. (Electrons $\times 10$)

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 0**																			
4	0	1220	1649	2	6	-490	-446	1	14	200	267	4	3	640	573	10	9	318	313
6	0	788	664	3	6	248	24	2	14	333	297	5	3	1131	1064	11	9	-414	-390
8	0	1621	1319	4	6	580	385	4	14	757	720	7	3	351	284	12	9	358	369
10	0	2145	2222	5	6	618	385	5	14	-275	-321	8	3	-600	-469	13	9	-274	-291
12	0	1135	1376	8	6	268	423	6	14	719	734	9	3	244	263	15	9	-114	-123
14	0	993	1006	9	6	-418	-469	7	14	-268	-343	10	3	-495	-502	17	9	-200	-177
16	0	605	620	10	6	653	587	8	14	682	761	11	3	-160	-141	1	10	-1023	-1018
18	0	391	335	11	6	-1100	-1080	10	14	343	322	12	3	-486	-536	2	10	-170	-209
20	0	423	394	12	6	173	97	14	14	283	224	13	3	-232	-254	3	10	-929	-885
4	1	174	72	15	6	273	229	16	14	297	396	14	3	-339	-349	4	10	-112	-135
5	1	417	456	16	6	223	159	17	14	-276	-339	15	3	-92	-76	5	10	-735	-748
6	1	1587	1254	19	6	-348	-385	1	15	620	711	16	3	88	90	7	10	-626	-701
7	1	1658	1374	21	6	-450	-393	3	15	197	103	18	3	-119	-106	8	10	70	69
8	1	828	645	1	7	-693	-663	8	15	-252	-343	19	3	198	150	9	10	-810	-843
9	1	1469	1403	2	7	704	409	9	15	359	377	1	4	-1205	-1154	10	10	-79	-76
10	1	-1892	-1684	7	7	254	319	11	15	208	262	2	4	-452	-272	11	10	-401	-375
11	1	1318	1376	8	7	347	332	16	15	-232	-260	3	4	-41	-44	12	10	-69	-75
12	1	-1531	-1551	9	7	-296	-215	0	16	740	671	4	4	778	646	17	10	-368	-352
13	1	416	447	10	7	-505	-487	1	16	-273	-169	5	4	319	292	0	11	-768	-939
14	1	-1071	-1028	12	7	-648	-653	2	16	233	297	6	4	489	447	2	11	-1088	-1020
15	1	197	138	15	7	252	249	3	16	266	204	7	4	-170	-146	4	11	-882	-973
18	1	-354	-323	16	7	365	280	4	16	-253	-293	8	4	122	146	6	11	-1069	-1095
20	1	-407	-473	17	7	-247	-240	5	16	454	391	9	4	-632	-590	8	11	-810	-854
22	1	-357	-375	20	7	-270	-238	6	16	-521	-490	10	4	-4	-3	9	11	468	437
4	2	-2099	-2107	0	8	-1861	-1870	7	16	344	340	11	4	-298	-349	10	11	-796	-858
5	2	-1115	-853	1	8	-335	-259	9	16	-335	-339	13	4	-204	-235	11	11	439	429
6	2	-1256	-1145	2	8	-936	-953	11	16	-325	-308	14	4	-31	-28	12	11	-417	-406
7	2	315	402	3	8	504	541	12	16	242	254	16	4	-76	-75	13	11	178	147
8	2	-1274	-1295	5	8	309	83	1	17	-540	-537	18	4	-147	-129	14	11	-329	-356
9	2	-206	-142	6	8	-360	-353	3	17	-382	-371	19	4	-140	-134	16	11	-449	-431
10	2	-1073	-1021	8	8	324	231	10	17	-452	-390	0	5	-994	-967	1	12	-169	-172
11	2	-237	-310	9	8	423	450	0	18	-529	-570	1	5	-311	-334	2	12	315	213
12	2	-658	-490	11	8	260	365	2	18	-580	-570	2	5	-1287	-1227	3	12	-164	-111
14	2	-392	-457	13	8	469	475	4	18	-463	-464	3	5	1164	1093	5	12	-194	-190
15	2	352	318	15	8	529	560	6	18	-587	-582	4	5	458	417	7	12	-35	-29
16	2	-318	-410	19	8	338	418	8	18	-705	-612	5	5	767	560	8	12	291	252
18	2	-208	-123	20	8	453	498	10	18	-370	-399	6	5	228	208	9	12	-63	-87
21	2	-310	-273	2	9	277	227	12	18	-342	-331	7	5	-441	-369	10	12	206	210
1	3	-1105	-1315	3	9	707	506	1	19	-464	-405	8	5	-366	-378	11	12	-265	-294
2	3	-574	-736	4	9	392	271	3	19	-399	-442	9	5	-395	-365	12	12	65	71
3	3	3029	-2724	5	9	457	140	5	19	-349	-353	10	5	-351	-402	13	12	-356	-285
5	3	-1288	-1193	6	9	380	353	6	19	294	187	14	5	240	251	0	13	617	676
6	3	843	837	7	9	-249	-27	7	19	-317	-220	17	5	-177	-181	2	13	339	340
7	3	-1289	-1341	8	9	292	428	8	19	430	440	19	5	-212	-245	3	13	-16	-16
8	3	1223	1089	9	9	451	510	10	19	387	358	1	6	-895	-1060	4	13	448	492
9	3	-1008	-1143	10	9	1277	1305	0	20	362	411	2	6	269	283	5	13	-50	-34
10	3	934	896	11	9	458	457	3	20	-250	-220	3	6	-509	-385	6	13	641	631
11	3	-1419	-1360	12	9	908	1040	6	20	230	107	4	6	688	724	8	13	544	516
12	3	-255	-90	14	9	594	607	1	21	505	519	5	6	417	421	9	13	-103	-98
13	3	-783	-876	16	9	483	485	3	21	414	390	6	6	-592	-643	10	13	300	290
14	3	-296	-294	18	9	567	573	5	21	304	300	8	6	-799	-775	11	13	-187	-114
15	3	-563	-531	19	9	252	234	9	21	301	300	9	6	-301	-256	14	13	218	187
17	3	-282	-405	20	9	570	666	5	0	511	365	10	6	-121	-198	1	14	225	251
18	3	230	270	0	10	1305	1243	7	0	-798	-811	11	6	-43	-43	2	14	-40	-43
19	3	-200	-180	2	10	1234	1389	9	0	-699	-672	12	6	220	199	3	14	519	565
20	3	396	379	3	10	-508	-464	11	0	259	269	15	6	261	254	4	14	-165	-163
22	3	274	237	5	10	-585	-626	13	0	436	418	16	6	-263	-220	5	14	460	472
0	4	351	454	6	10	485	463	15	0	500	513	0	7	1039	1011	6	14	32	31
1	4	-930	-717	7	10	439	514	17	0	258	275	1	7	532	311	7	14	667	671
2	4	-1224	-1172	8	10	541	609	19	0	373	370	2	7	100	91	9	14	468	405
4	4	-1292	-1247	9	10	532	695	4	1	802	778	3	7	655	698	0	15	142	118
5	4	-1273	-1265	10	10	483	528	5	1	1169	929	4	7	371	441	1	15	63	40
6	4	285	82	11	10	300	304	6	1	-427	-392	5	7	265	354	2	15	118	133
7	4	198	246	17	10	287	255	7	1	263	257	6	7	328	358	4	15	206	116
9	4	919	871	19	10	217	253	8	1	-271	-133	7	7	-666	-672	8	15	-67	-81
11	4	-542	-449	20	10	-245	-246	9	1	259	282	8	7	365	403	10	15	-99	-89
12	4	-484	-401	2	11	-678	-503	10	1	750	692	9	7	-308	-305	1	16	-197	-187
13	4	-185	-142	4	11	-297	-373	11	1	388	401	10	7	550	619	2	16	410	424
15	4	-371	-450	6	11	-196	-170	12	1	292	256	11	7	183	216	3	16	-276	-250
17	4	-218	-240	7	11	-305	-264	13	1	97	104	12	7	287	286	5	16	-290	-302
18	4	-237	-248	9	11	-343	-399	14	1	235	209	13	7	460	424	6	16	106	75
20	4	-262	-243	10	11	-553	-517	16	1	86	84	14	7	124	138	7	16	-210	-256
21	4	290	320	11	11	-351	-383	17	1	365	317	1	8	1572	1607	9	16	-146	-145
22	4	-204	-204	12	11	-891	-928	18	1	-68	-57	2	8	378	203	10	16	90	104
2	5	-168	-81	13	11	-331	-320	19	1	439	445	3	8	1089	1211	0	17	168	135
3	5	851	757	14	11	-351	-383	4	2	-499	-399	4	8	47	66	2	17	-117	-117
4	5	272	39	0	12	-846	-906	5	2	314	167	5	8	496	458	3	17	230	218
5	5	-437	-479	2	12	-874	-796	6	2	112	131	7	8	966	924	4	17	-293	-333
6	5	-550	-575	5	12	462	269	8	2	256	389	8	8	-363	-319	6	17	-253	-234
7	5	374	411	6	12	-622	-604	9	2	86	92	9	8	1023	1033	8	17	157	178
8	5	-238	-236	12	12	-515	-501	10	2	507	479	10	8	-166	-168	10	17	191	160
10	5	-403	-407	10	12	-583	-618	11	2	-150	-158	11	8	77					

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
4	0	969	858	8	6	383	405	5	14	276	248	0	5	-41	-35	15	11	-189	-196
6	0	370	378	12	6	-152	-119	6	14	187	179	1	5	92	100	1	12	-351	-334
8	0	-421	-387	13	6	-56	-43	8	14	86	85	2	5	-161	-48	2	12	-654	-579
10	0	181	222	16	6	23	23	14	14	213	162	3	5	284	335	3	12	-117	-149
12	0	74	83	17	6	-379	-380	2	15	237	158	4	5	251	310	4	12	-62	-62
18	0	375	375	1	7	252	254	3	15	184	217	5	5	-120	-121	5	12	15	14
20	0	410	417	3	7	-169	-153	4	15	234	225	6	5	240	237	7	12	-97	-91
4	1	-8	-10	4	7	-157	-108	5	15	287	266	7	5	-181	-168	9	12	-371	-392
5	1	-421	-308	5	7	-351	-383	7	15	333	231	8	5	815	748	12	12	-118	-91
6	1	350	330	7	7	-370	-344	11	15	-38	-37	12	5	-202	-183	0	13	-112	-110
7	1	-42	-47	8	7	-246	-273	13	15	-37	-35	14	5	-26	-22	2	13	2	2
8	1	442	384	9	7	202	206	0	16	-293	-303	16	5	363	374	4	13	347	355
9	1	86	57	10	7	6	7	1	16	142	93	18	5	470	478	8	13	-178	-177
10	1	797	764	11	7	251	237	3	16	253	245	1	6	-191	-199	9	13	253	212
11	1	167	160	12	7	489	506	6	16	242	230	2	6	279	234	10	13	-133	-171
12	1	430	431	13	7	39	41	7	16	-151	-133	3	6	-625	-655	11	13	183	129
13	1	-34	-33	14	7	209	195	9	16	213	91	4	6	128	104	1	14	49	42
14	1	-26	-25	17	7	4	4	11	16	58	61	5	6	-438	-450	2	14	247	298
15	1	-23	-23	18	7	-175	-148	1	17	155	124	6	6	-7	-9	3	14	65	54
16	1	-80	-80	0	8	1266	1306	2	17	-176	-163	7	6	106	116	4	14	288	289
18	1	122	117	1	8	407	345	4	17	-22	-19	8	6	-66	-56	5	14	194	202
19	1	323	205	2	8	647	693	5	17	-153	-151	9	6	115	104	12	14	10	12
20	1	225	244	3	8	4	6	0	18	468	453	10	6	-123	-148	0	15	-188	-197
4	2	-557	-395	4	8	-81	-80	4	18	225	177	11	6	98	89	2	15	-168	-154
5	2	488	309	6	8	-271	-270	2	19	51	41	12	6	-104	-113	3	15	270	318
6	2	-779	-705	7	8	-97	-71	4	19	-37	-46	13	6	-340	-346	4	15	-262	-267
7	2	623	593	8	8	-9	-8	**L = 3****				16	6	138	137	6	15	-223	-213
8	2	-440	-484	10	8	378	410	5	0	75	82	17	6	-105	-106	7	15	-213	-295
9	2	904	960	11	8	-154	-127	7	0	400	409	18	6	-154	-177	8	15	81	89
10	2	-246	-249	12	8	380	379	9	0	1121	1040	0	7	-301	-293	9	15	-264	-274
11	2	247	255	14	8	300	258	11	0	621	576	1	7	-88	-102	10	15	-2	-2
13	2	-85	-88	18	8	-61	-60	13	0	-213	-193	2	7	-964	-988	1	16	-83	-68
14	2	-219	-94	1	9	427	438	17	0	-139	-145	3	7	-346	-381	3	16	-184	-189
15	2	-90	-107	2	9	-263	-259	19	0	181	185	4	7	-626	-630	5	16	-368	-333
17	2	78	92	4	9	100	82	4	1	180	189	5	7	-557	-516	6	16	179	87
18	2	-254	-294	5	9	-101	-117	5	1	-246	-233	6	7	-537	-583	7	16	-51	-51
19	2	201	204	6	9	-224	-277	6	1	249	255	7	7	-173	-116	9	16	-10	-11
1	3	-644	-558	7	9	245	191	7	1	280	255	8	7	-649	-669	0	17	-209	-271
2	3	376	345	8	9	-150	-145	8	1	545	559	9	7	-193	-249	3	17	-238	-271
3	3	-464	-488	9	9	335	352	9	1	-284	-300	10	7	-457	-448	4	17	121	92
5	3	-448	-463	10	9	-752	-651	10	1	-74	-83	12	7	-301	-335	7	17	-196	-112
6	3	229	229	11	9	246	347	11	1	-940	-991	14	7	-197	-210	1	18	17	17
7	3	-744	-720	12	9	-614	-665	13	1	-1124	-1089	16	7	-130	-147	3	18	-117	-97
8	3	493	499	13	9	205	124	15	1	-745	-800	17	7	-102	-105	5	18	-180	-252
9	3	-803	-798	14	9	-177	-179	16	1	-265	-299	1	8	-443	-455	**L = 4****			
12	3	0	0	16	9	-93	-86	17	1	-603	-642	3	8	-835	-795	4	0	-158	-167
13	3	-135	-112	17	9	-147	-113	19	1	-472	-502	4	8	533	486	6	0	-1417	-1346
15	3	198	177	0	10	-475	-464	4	2	-105	-110	5	8	-602	-569	8	0	-923	-972
16	3	202	193	1	10	-457	-317	5	2	-702	-705	6	8	-95	-89	10	0	-747	-718
18	3	237	266	2	10	-743	-789	6	2	-387	-321	7	8	-801	-795	12	0	-208	-203
0	4	-451	-482	3	10	-300	-306	7	2	-1038	-1047	8	8	114	64	16	0	-340	-277
1	4	909	745	4	10	139	135	8	2	-118	-110	9	8	-645	-750	4	1	347	384
2	4	112	105	6	10	-399	-409	9	2	-726	-682	11	8	-231	-211	5	1	-190	-236
3	4	600	614	7	10	-157	-171	10	2	-127	-110	13	8	-175	-195	6	1	303	287
4	4	566	520	8	10	-190	-192	11	2	-181	-192	14	8	283	271	7	1	-777	-716
5	4	735	679	10	10	-228	-210	12	2	-297	-337	15	8	5	4	8	1	173	152
6	4	205	230	11	10	-383	-370	13	2	151	147	0	9	389	376	9	1	-372	-364
7	4	423	369	12	10	-192	-169	14	2	-474	-487	1	9	395	441	10	1	178	191
8	4	307	295	14	10	-238	-301	16	2	-319	-339	2	9	236	219	11	1	132	87
9	4	-290	-283	16	10	-77	-84	17	2	-284	-273	3	9	400	494	12	1	79	78
10	4	-175	-195	1	11	-495	-506	18	2	-246	-249	4	9	-180	-210	13	1	44	39
11	4	160	154	2	11	-460	-468	19	2	-232	-127	5	9	278	274	14	1	-92	-86
12	4	33	32	3	11	-391	-410	1	3	582	605	6	9	32	33	16	1	142	118
14	4	3	4	4	11	-174	-191	2	3	-289	-293	7	9	401	358	17	1	-368	-370
15	4	256	237	5	11	-431	-416	3	3	434	448	8	9	352	358	18	1	257	270
16	4	176	166	6	11	148	142	4	3	-220	-223	9	9	240	249	4	2	416	432
17	4	310	345	7	11	-203	-211	5	3	-239	-264	10	9	459	507	5	2	-350	-315
18	4	173	153	8	11	382	437	6	3	11	10	11	9	421	425	6	2	177	160
19	4	186	204	9	11	-413	-406	8	3	-199	-209	12	9	337	369	7	2	-27	-28
1	5	236	268	10	11	279	278	9	3	442	452	13	9	542	531	8	2	545	617
2	5	312	262	11	11	-411	-383	10	3	-364	-335	15	9	362	359	9	2	20	16
3	5	581	515	12	11	123	117	11	3	273	225	1	10	1265	1371	10	2	482	413
4	5	463	413	13	11	-430	-367	12	3	25	23	3	10	768	770	11	2	193	189
5	5	1071	1017	14	11	-199	-173	14	3	173	208	4	10	-380	-390	12	2	-93	-97
6	5	12	27	15	11	-242	-249	15	3	-50	-47	5	10	526	517	13	2	45	39
7	5	1028	1041	0	12	-137	-146	18	3	-69	-58	7	10	503	557	15	2	-183	-214
8	5	-44	-44	1	12	-373	-456	19	3	132	151	8	10	162	176	1	3	594	640
9	5	639	573	2	12	-341	-333	1	4	308	292	9	10	935	832	2	3	-317	-283
10	5	-243	-145	3	12	-254	-253	2	4	530	488	10	10	207	224	3	3	938	869
11	5	-3	-3	7	12	318	358	3	4	152	181	11	10	567	591	4	3	-277	-260
12	5	-376	-288	8	12	-220	-183	4	4	188	169	13	10	-67	-73	5	3	572	622
15	5	246	241	9	12	537	522	5	4	767	791	16	10	287	247	6	3	41	43
17	5	41	36	10	12	-243	-273	6	4	-32	-41	0	11	489	501	7	3	684	690
18	5	76	61	14	12	-32	-39	7	4	690	675	1	11	-360	-366	8	3	123	116

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
2	4	-73	-80	2	12	272	364	10	4	594	583	2	14	-13	-12	5	11	301	290
3	4	-575	-647	3	12	323	372	11	4	336	341	3	14	-257	-243	7	11	272	251
4	4	1001	1096	4	12	315	334	12	4	552	496	5	14	-220	-260	9	11	242	201
5	4	-167	-171	5	12	215	281	13	4	318	255	8	14	235	223	0	12	-225	-209
6	4	465	454	6	12	585	610	14	4	343	364	0	15	98	81	1	12	-58	-35
7	4	285	285	8	12	453	450	15	4	330	337	**L = 6****				2	12	67	59
8	4	327	349	9	12	241	204	16	4	318	283	4	0	-294	-313	7	12	155	143
9	4	32	26	11	12	303	256	0	5	1078	1108	6	0	381	354	1	13	-89	-84
10	4	173	168	13	12	233	230	1	5	127	128	8	0	239	260	3	13	28	27
11	4	-174	-132	1	13	320	321	2	5	733	689	12	0	-78	-65	**L = 7****			
12	4	189	187	2	13	-126	-94	4	5	438	477	3	1	-108	-108	3	0	-200	-313
13	4	-295	-330	3	13	175	165	5	5	67	114	4	1	-201	-212	5	0	-113	-116
14	4	418	414	5	13	390	349	6	5	518	503	5	1	37	29	7	0	-214	-187
15	4	-390	-420	7	13	353	371	8	5	402	371	6	1	-154	-187	9	0	-137	-143
16	4	317	343	9	13	251	289	9	5	303	288	7	1	-37	-38	11	0	-117	-136
17	4	-243	-278	0	14	-319	-373	10	5	432	421	10	1	-190	-202	3	1	0	0
1	5	-411	-418	2	14	-330	-301	12	5	500	442	12	1	-488	-440	4	1	-40	-46
2	5	215	172	3	14	-214	-216	13	5	223	87	13	1	-314	-341	6	1	-60	-54
3	5	-155	-156	4	14	-96	-78	14	5	274	337	14	1	-140	-161	8	1	-153	-147
5	5	215	217	7	14	-99	-88	2	6	-4	-4	3	2	-50	-53	9	1	272	281
7	5	-325	-295	9	14	-191	-185	3	6	-112	-114	6	2	-205	-257	11	1	144	134
9	5	-314	-282	10	14	-293	-221	4	6	92	82	8	2	-329	-317	3	2	240	261
11	5	62	63	1	15	-520	-509	6	6	-178	-122	10	2	-165	-118	4	2	-73	-77
12	5	190	184	3	15	-370	-324	8	6	-301	-284	11	2	-137	-143	5	2	181	175
13	5	281	285	4	15	31	31	10	6	-418	-385	13	2	-103	-84	7	2	160	195
15	5	425	356	5	15	-380	-393	12	6	-227	-232	1	3	131	138	9	2	260	268
0	6	-1192	-1218	6	15	-340	-265	14	6	36	31	5	3	233	230	10	2	208	146
1	6	67	65	7	15	-506	-512	15	6	-9	-6	7	3	153	122	11	2	235	235
2	6	-380	-331	8	15	-154	-165	0	7	-616	-596	10	3	162	172	0	3	518	789
3	6	532	556	9	15	-538	-540	1	7	52	63	12	3	122	158	1	3	-147	-247
4	6	-685	-744	0	16	-243	-169	2	7	-553	-547	13	3	265	141	2	3	253	285
5	6	188	157	1	16	205	180	3	7	273	248	0	4	381	371	3	3	-178	-192
6	6	-486	-535	2	16	-393	-399	4	7	-441	-437	2	4	263	279	4	3	263	246
8	6	-434	-398	3	16	296	279	6	7	-598	-625	4	4	316	335	6	3	-74	-78
9	6	-42	-29	4	16	-293	-229	7	7	-216	-244	6	4	384	395	8	3	295	312
10	6	-383	-386	6	16	-395	-373	8	7	-357	-325	7	4	-162	-172	10	3	272	280
11	6	315	394	1	17	239	226	9	7	-288	-291	8	4	317	315	11	3	-270	-270
13	6	515	469	2	17	320	179	10	7	-504	-468	9	4	148	99	12	3	218	171
15	6	199	142	4	17	294	221	11	7	-304	-281	10	4	196	217	1	4	-121	-156
17	6	309	271	**L = 5****				13	7	71	66	11	4	-95	-92	2	4	-255	-271
1	7	-468	-489	3	0	-531	-620	14	7	-329	-328	12	4	190	160	3	4	-41	-35
2	7	427	405	5	0	-696	-691	1	8	-262	-261	13	4	-26	-24	5	4	30	32
3	7	-491	-555	7	0	-506	-492	3	8	-291	-325	1	5	3	4	7	4	-60	-50
4	7	468	455	9	0	-668	-626	4	8	-132	-36	3	5	219	192	10	4	-277	-226
5	7	-320	-314	11	0	-483	-465	6	8	-100	-94	5	5	238	267	0	5	-511	-561
7	7	-300	-247	15	0	-127	-132	7	8	-235	-206	7	5	206	192	2	5	-457	-463
8	7	-266	-247	3	1	403	397	8	8	-159	-111	8	5	-119	-117	4	5	-145	-163
9	7	-189	-207	4	1	-475	-517	9	8	-241	-231	9	5	109	67	5	5	68	57
11	7	-223	-192	6	1	-672	-636	11	8	-194	-176	10	5	2	2	8	5	-336	-265
12	7	403	477	7	1	130	128	12	8	-133	-133	11	5	66	61	10	5	-237	-264
13	7	-488	-522	8	1	-231	-224	13	8	-281	-292	0	6	-171	-187	1	6	-579	-561
14	7	547	560	9	1	-180	-164	0	9	203	299	2	6	-197	-182	3	6	-314	-292
15	7	-282	-270	10	1	-166	-190	1	9	-97	-150	3	6	1	1	4	6	-6	-7
16	7	316	264	11	1	-132	-133	2	9	-40	-34	6	6	-173	-148	5	6	-150	-151
0	8	573	627	12	1	-230	-193	3	9	-200	-171	9	6	-43	-39	9	6	-129	-135
3	8	-81	-93	13	1	-192	-185	4	9	123	118	10	6	1	1	10	6	274	256
5	8	56	23	14	1	-371	-314	5	9	-408	-431	11	6	50	45	0	7	-1	-1
6	8	-8	-8	16	1	-161	-172	6	9	-163	-139	1	7	-302	-313	1	7	-239	-268
8	8	226	203	3	2	-396	-422	10	9	195	225	2	7	-223	-221	2	7	87	80
9	8	-203	-119	5	2	11	11	11	9	-105	-104	3	7	-355	-324	9	7	226	240
12	8	-214	-235	6	2	165	156	13	9	-275	-265	5	7	-329	-333	1	8	434	506
14	8	-330	-316	7	2	145	148	1	10	389	391	6	7	-233	-291	3	8	257	279
2	9	-586	-520	8	2	96	156	2	10	-293	-308	7	7	-316	-312	5	8	-84	-75
4	9	-545	-531	9	2	27	29	3	10	122	115	8	7	31	30	7	8	-69	-74
5	9	183	161	10	2	-181	-180	4	10	-175	-144	9	7	-306	-311	4	9	138	130
6	9	-137	-163	11	2	-46	-39	5	10	-50	-52	10	7	70	72	5	9	166	200
7	9	211	228	12	2	-407	-421	6	10	-219	-208	11	7	-268	-266	6	9	141	143
8	9	32	34	13	2	-300	-254	7	10	-10	-11	12	7	-53	-43	8	9	183	190
9	9	30	32	15	2	35	19	9	10	77	83	0	8	-385	-413	1	10	-234	-207
10	9	-343	-292	0	3	-290	-355	11	10	217	222	2	8	-278	-253	7	10	-36	-20
11	9	270	197	1	3	-151	-147	0	11	341	360	3	8	217	276	0	11	-94	-85
12	9	-455	-411	2	3	-42	-55	1	11	124	138	4	8	-256	-225	2	11	-67	-74
14	9	-387	-407	3	3	-56	-58	2	11	372	420	6	8	-607	-609	4	11	79	99
16	9	-337	-336	4	3	496	479	7	11	119	100	7	8	-107	-115	**L = 8****			
0	10	44	44	5	3	76	79	8	11	-20	-18	8	8	-596	-542	4	0	253	231
3	10	-306	-282	6	3	403	416	9	11	-3	-3	10	8	-317	-351	6	0	8	8
4	10	-16	-18	7	3	169	102	11	11	-53	-87	12	8	-126	-156	3	1	35	43
7	10	-129	-133	8	3	325	288	12	11	211	231	3	9	37	41	5	1	29	37
8	10	-331	-299	10	3	56	59	1	12	-97	-90	4	9	313	280	3	2	33	33
9	10	-115	-160	11	3	234	247	2	12	37	25	5	9	-108	-122	4	2	-86	-73
10	10	-114	-116	13	3	208	204	3	12	61	74	6	9	16	14	6	2	42	52
15	10	-171	-148	14	3	206	227	4	12	-50	-51	7	9	-4	-3	1	3	-309	-414
2	11	194	188	15	3	113	89	5	12	210	211	8	9	-126	-114	2	3	58	70
3	11	187	149	16	3	210	127	6	12	201	150	9	9	204	181	3	3	-168	

TABLE 4

Atomic Coordinates and Isotropic Temperature Factors

Atom	x	y	z	B
Fe1	-0.0043(2)	0.1380(2)	0.1000	3.9*
Fe2	0.0128(2)	0.1956(2)	0.3600(6)	3.9*
S1	0.1119(3)	0.1983(4)	0.3581(11)	4.3*
S2	0.0169(3)	0.2971(4)	0.3246(10)	4.9*
S3	0.0923(4)	0.1154(4)	0.0325(10)	4.7*
S4	0.0049(4)	0.2226(4)	-0.0341(10)	5.2*
S5	-0.0757(3)	0.1910(3)	0.2210(10)	4.1*
S6	0.0148(3)	0.0889(3)	0.2987(10)	4.0*
N1	-0.0415(11)	0.0923(13)	0.0138(30)	5.5(6)
O1	-0.0653(13)	0.0553(14)	-0.0695(33)	9.9(8)
N2	-0.0132(12)	0.1831(12)	0.5169(28)	5.2(6)
O2	-0.0318(13)	0.1766(14)	0.6346(34)	9.4(8)
C1	0.1355(12)	0.2725(13)	0.3337(30)	3.9(6)
C2	0.0930(12)	0.3221(12)	0.3229(27)	3.6(6)
C3	0.1198(13)	0.0674(13)	0.1690(29)	3.8(6)
C4	-0.0551(13)	0.2702(13)	0.0209(33)	4.0(6)
C5	-0.0892(12)	0.2569(12)	0.1254(27)	3.2(6)
C6	0.0910(13)	0.0565(13)	0.2812(31)	3.6(7)
CL1	-0.2854(14)	0.1730(14)	0.3436(38)	14.0(10)
CL2	-0.3945(13)	0.1782(14)	0.1966(30)	12.4(8)

* These values are equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters shown in Table 5.

(Continued on next page)

Table 4 continued

Rigid Bodies

(a) Phenyl Carbon Atoms

Atom	x	y	z	B
C11	0.2007 (7)	0.2856 (7)	0.3191 (16)	3.3 (6)
C12	0.2390 (7)	0.2483 (7)	0.2359 (16)	6.3 (8)
C13	0.3025 (7)	0.2561 (7)	0.2425 (16)	7.2 (9)
C14	0.3277 (7)	0.3013 (7)	0.3325 (16)	6.2 (8)
C15	0.2894 (7)	0.3387 (7)	0.4157 (16)	5.8 (8)
C16	0.2259 (7)	0.3309 (7)	0.4090 (16)	5.2 (8)
D	0.7473 (1)			
E	0.0654 (1)			
F	3.3044 (1)			
C21	0.1079 (6)	0.3868 (7)	0.2876 (16)	5.2 (7)
C22	0.1504 (6)	0.4025 (7)	0.1833 (16)	5.3 (7)
C23	0.1610 (6)	0.4657 (7)	0.1498 (16)	6.0 (8)
C24	0.1292 (6)	0.5133 (7)	0.2207 (16)	8.1 (10)
C25	0.0867 (6)	0.4976 (7)	0.3251 (16)	6.6 (8)
C26	0.0761 (6)	0.4343 (7)	0.3585 (16)	4.3 (6)
D	6.2448 (2)			
E	0.8101 (2)			
F	4.4296 (1)			

(Continued on next page)

Table 4 continued

Atom	x	y	z	B
C31	0.1857(7)	0.0499(6)	0.1548(17)	3.0(6)
C32	0.2282(7)	0.0596(6)	0.2626(17)	6.4(8)
C33	0.2891(7)	0.0411(6)	0.2444(17)	8.6(10)
C34	0.3076(7)	0.0129(6)	0.1184(17)	6.6(8)
C35	0.2651(7)	0.0032(6)	0.0106(17)	6.7(8)
C36	0.2041(7)	0.0217(6)	0.0288(17)	6.0(8)
D	5.1617(1)			
E	2.6209(3)			
F	0.7011(3)			
C41	-0.0556(5)	0.3291(6)	-0.0780(19)	4.3(7)
C42	-0.0538(5)	0.3290(6)	-0.2250(19)	4.9(8)
C43	-0.0529(5)	0.3860(6)	-0.2986(19)	7.2(9)
C44	-0.0537(5)	0.4431(6)	-0.2254(19)	8.5(11)
C45	-0.0555(5)	0.4432(6)	-0.0784(19)	6.4(9)
C46	-0.0564(5)	0.3862(6)	-0.0047(19)	4.2(7)
D	0.0010(1)			
E	1.5435(1)			
F	4.1872(1)			

(Continued on next page)

Table 4 continued

Atom	x	y	z	B
C51	-0.1431 (6)	0.2964 (6)	0.1740 (16)	4.9 (7)
C52	-0.1455 (6)	0.3107 (6)	0.3174 (16)	5.2 (7)
C53	-0.1959 (6)	0.3432 (6)	0.3721 (16)	8.7 (10)
C54	-0.2437 (6)	0.3615 (6)	0.2833 (16)	5.1 (7)
C55	-0.2413 (6)	0.3471 (6)	0.1399 (16)	5.3 (8)
C56	-0.1910 (6)	0.3146 (6)	0.0852 (16)	6.2 (7)
D	2.0886 (2)			
E	1.9325 (3)			
F	1.5011 (3)			
C61	0.1081 (7)	0.0252 (8)	0.4091 (20)	5.4 (8)
C62	0.0899 (7)	0.0389 (8)	0.5467 (20)	7.4 (9)
C63	0.1111 (7)	0.0019 (8)	0.6583 (20)	9.7 (11)
C64	0.1506 (7)	-0.0486 (8)	0.6323 (20)	6.6 (8)
C65	0.1688 (7)	-0.0622 (8)	0.4947 (20)	13.3 (16)
C66	0.1476 (7)	-0.0253 (8)	0.3831 (20)	9.1 (12)
D	5.6295 (1)			
E	1.4374 (2)			
F	0.7840 (1)			

(Continued on next page)

Table 4 continued

(b) Phenyl Hydrogen Atoms

Atom	x	y	z	B
H12	0.2194	0.2163	0.1730	6.6
H13	0.3285	0.2283	0.1815	8.0
H14	0.3735	0.3055	0.3343	6.7
H15	0.3093	0.3706	0.4786	5.7
H16	0.2001	0.3585	0.4701	5.2
D	0.7464			
E	0.0653			
F	4.3346			
H22	0.1719	0.3673	0.1360	5.8
H23	0.1913	0.4753	0.0755	6.1
H24	0.1376	0.5581	0.1948	8.4
H25	0.0644	0.5331	0.3745	6.7
H26	0.0450	0.4251	0.4349	4.1
D	6.2444			
E	0.8100			
F	5.4597			

(Continued on next page)

Table 4 continued

Atom	x	y	z	B
H32	0.2130	0.0797	0.3514	7.0
H33	0.3180	0.0487	0.3241	8.9
H34	0.3513	0.0002	0.1095	6.4
H35	0.2798	-0.0172	-0.0779	7.1
H36	0.1748	0.0138	-0.0507	6.7
D	5.1618			
E	2.6205			
F	1.7313			
H42	-0.0535	0.2869	-0.2741	5.4
H43	-0.0518	0.3837	-0.4042	7.1
H44	-0.0531	0.4827	-0.2822	9.0
H45	-0.0561	0.4848	-0.0300	7.0
H46	-0.0577	0.3879	0.1001	4.5
D	0.0013			
E	1.5440			
F	5.2173			
H52	-0.1103	0.2968	0.3743	5.6
H53	-0.1958	0.3526	0.4720	9.5

(Continued on next page)

Table 4 continued

Atom	x	y	z	B
H54	-0.2789	0.3847	0.3232	5.3
H55	-0.2764	0.3610	0.0765	5.8
H56	-0.1908	0.3052	-0.0213	6.2
D	2.0890			
E	1.9330			
F	2.5315			
H62	0.0611	0.0755	0.5608	7.6
H63	0.0965	0.0132	0.7551	10.0
H64	0.1643	-0.0739	0.7148	6.9
H65	0.1967	-0.0987	0.4801	13.5
H66	0.1613	-0.0364	0.2859	9.1
D	5.6294			
E	1.4369			
F	1.8141			

D, E and F are the angles by which the coordinates of the individual atoms of the rigid body are rotated with respect to a set of axes X, Y, Z. The origin of these axes is placed at the centre of the ring with the X axis parallel to a^* , the Z axis parallel to c , and the Y axis parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing b and c .

Table 5

Anisotropic Temperature Factors ($\text{\AA}^2$)

Atom	U_{11}	U_{22}	U_{23}	U_{12}	U_{13}	U_{23}
Fe1	0.036(2)	0.046(2)	0.065(2)	-0.003(2)	-0.005(3)	-0.004(3)
Fe2	0.034(2)	0.047(3)	0.067(3)	-0.002(2)	0.000(3)	-0.006(3)
S1	0.042(4)	0.039(4)	0.082(5)	-0.003(4)	-0.007(5)	0.006(5)
S2	0.044(4)	0.049(5)	0.092(7)	-0.001(4)	-0.006(5)	-0.012(5)
S3	0.046(5)	0.060(5)	0.072(5)	0.014(4)	-0.004(4)	0.004(5)
S4	0.056(5)	0.055(5)	0.085(6)	0.013(5)	0.015(5)	0.000(5)
S5	0.032(4)	0.042(4)	0.082(6)	-0.002(4)	-0.011(4)	0.001(5)
S6	0.030(4)	0.042(4)	0.079(5)	-0.004(4)	-0.005(4)	0.005(4)

Table 6
Interatomic Distances

<u>Atoms</u>	<u>Distance Å</u> ^o	<u>Atoms</u>	<u>Distance Å</u> ^o
Fe1 - Fe2	2.780 (6)	S4 - C4	1.73 (3)
Fe1 - S3	2.253 (9)	S5 - C5	1.69 (3)
Fe1 - S4	2.208 (9)	S6 - C6	1.81 (3)
Fe1 - S5	2.238 (9)	N1 - O1	1.23 (3)
Fe1 - S6	2.195 (9)	N2 - O2	1.20 (3)
Fe2 - S1	2.163 (8)	C1 - C2	1.40 (3)
Fe2 - S2	2.181 (9)	C3 - C6	1.26 (3)
Fe2 - S5	2.340 (8)	C4 - C5	1.27 (3)
Fe2 - S6	2.335 (8)	C1 - C11	1.46 (3)
Fe1 - N1	1.51 (3)	C2 - C21	1.45 (3)
Fe2 - N2	1.62 (3)	C3 - C31	1.49 (3)
S1 - C1	1.67 (3)	C4 - C41	1.56 (3)
S2 - C2	1.74 (3)	C5 - C51	1.51 (3)
S3 - C3	1.76 (3)	C6 - C61	1.43 (3)

Table 7
Intramolecular Angles

<u>Atoms</u>	<u>Angles</u>	<u>Atoms</u>	<u>Angles</u>
S6 - Fe1 - S5	85.9(4)	N1 - Fe1 - S4	105(1)
S6 - Fe1 - S3	88.1(3)	N1 - Fe1 - S5	103(1)
S4 - Fe1 - S3	85.6(3)	N1 - Fe1 - S6	105(1)
S4 - Fe1 - S5	87.2(3)	N2 - Fe2 - S1	111(1)
S5 - Fe2 - S6	80.5(3)	N2 - Fe2 - S2	108(1)
S5 - Fe2 - S2	89.3(3)	N2 - Fe2 - S5	103(1)
S2 - Fe2 - S1	86.0(3)	N2 - Fe2 - S6	95(1)
S1 - Fe2 - S6	90.3(3)		
Fe1 - S5 - Fe2	74.7(3)	Fe2 - S1 - C1	110(1)
Fe1 - S6 - Fe2	75.6(3)	Fe2 - S2 - C2	110(1)
Fe1 - Fe2 - S1	97.9(3)	S1 - C1 - C2	121(2)
Fe1 - Fe2 - S2	107.6(3)	S2 - C2 - C1	114(2)
Fe1 - Fe2 - S5	51.0(2)	S1 - C1 - C11	120(2)
Fe1 - Fe2 - S6	49.9(2)	S2 - C2 - C21	120(2)
Fe2 - Fe1 - S4	98.3(3)	Fe2 - S5 - C5	114(1)
Fe2 - Fe1 - S3	102.8(3)	Fe1 - S5 - C5	105(1)
Fe2 - Fe1 - S5	54.3(2)	Fe1 - S4 - C4	103(1)
Fe2 - Fe1 - S6	54.5(2)	S4 - C4 - C5	123(2)
Fe1 - N1 - O1	171(3)	S5 - C5 - C4	120(2)
Fe2 - N2 - O2	177(3)	S4 - C4 - C41	107(2)
N1 - Fe1 - Fe2	147(1)	S5 - C5 - C51	115(2)
N2 - Fe2 - Fe1	135(1)	Fe2 - S6 - C6	114(1)
N1 - Fe1 - S3	102(1)	Fe1 - S3 - C3	103(1)

(continued on next page)

Table 7 continued

<u>Atoms</u>	<u>Angles</u>	<u>Atoms</u>	<u>Angles</u>
Fe1 - S6 - C6	106(1)	S2 - S5 - S6	90.9(3)
S3 - C3 - C6	124(2)	S2 - S4 - S3	94.7(3)
S6 - C6 - C3	118(2)	S2 - S1 - S6	91.8(3)
S3 - C3 - C31	114(2)	S2 - S1 - S3	99.8(3)
S6 - C6 - C61	110(2)	S4 - S2 - S1	81.3(3)
		S4 - S3 - S1	83.5(3)
S2 - S5 - S4	74.1(3)	S4 - S3 - S6	87.9(3)
S2 - S4 - S5	54.3(2)	S5 - S6 - S1	87.5(3)
S5 - S2 - S4	51.6(2)	S5 - S6 - S3	91.6(3)
S1 - S6 - S3	69.5(3)	S5 - S2 - S1	88.7(3)
S1 - S3 - S6	56.5(2)	S5 - S4 - S3	91.8(3)
S6 - S1 - S3	54.0(2)	S6 - S5 - S4	88.6(3)

Table 8Selected Intramolecular Non Bonded Contacts

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
S1	S2	2.96 (1)
S3	S6	3.09 (1)
S4	S5	3.07 (1)
S1	S6	3.19 (1)
S1	S3	3.58 (1)
S2	S5	3.18 (1)
S2	S4	3.77 (1)
S3	S4	3.03 (1)
S5	S6	3.02 (1)
CL1	CL2	2.76
CL1	Fe1	6.60 (3)
CL1	Fe2	6.52 (3)
O1	Fe1	2.73 (3)
O2	Fe2	2.81 (3)
N2	H62	2.83 (3)
O2	H62	3.03 (3)
S2	H52	2.82 (1)
H26	H46	3.97
H12	H32	3.36
H12	C32	3.43

Table 9
Intermolecular Contacts

<u>Atom 1</u>	<u>Atom 2</u>	<u>Symmetry Operation on2</u>	<u>Distance</u>
O1	H63	$\bar{x}, \bar{y}, z-1$	2.31(3)
O1	H36	$\bar{x}, \bar{y}, z$	2.81(3)
O2	H42	$x, y, z+1$	2.54(3)
O2	H14	$1/2+x-1, 1/2-y, 1/2+z$	2.83(3)
O2	S4	$x, y, z+1$	3.39(3)
CL1	H65	$\bar{x}, \bar{y}, z$	2.81(3)
CL1	H22	$1/2+x-1, 1/2-y, 1/2+z$	3.05(4)
CL2	H16	$1/2+x-1, 1/2-y, 1/2+z-1$	3.08(4)
H13	H42	$1/2+x, 1/2-y, 1/2+z$	2.63
H13	H53	$1/2+x, 1/2-y, 1/2+z-1$	2.68
H14	H42	$1/2+x, 1/2-y, 1/2+z$	2.73
H16	H35	$1/2-x, 1/2+y, 1/2+z$	2.71
H24	H46	$\bar{x}, \bar{y}+1, z$	2.27
H25	H26	$\bar{x}, \bar{y}+1, z$	2.61
H25	H43	$x, y+1, z+1$	2.76
H26	H43	$x, y, z+1$	2.75
H32	H55	$1/2+x, 1/2-y, 1/2+z$	2.49
H34	H44	$1/2+x, 1/2-y, 1/2+z$	2.35
H36	H63	$x, y, z-1$	2.51
H36	H54	$1/2+x, 1/2-y, 1/2+z-1$	2.66
H44	H44	$\bar{x}, \bar{y}+1, z$	2.43
H45	H45	$\bar{x}, \bar{y}+1, z$	2.53
H56	C13	$1/2+x-1, 1/2-y, 1/2+z-1$	2.60
H56	C14	$1/2+x-1, 1/2-y, 1/2+z-1$	2.68

Table 10Least Squares Planes

(1) Atoms defining plane: S3, S4, S5, S6

$$\text{Equation of plane } 0.5431X + 0.6446Y + 0.5380Z - 2.8810 = 0$$

<u>Atom</u>	<u>Deviation from Least Squares Plane (Å)</u>
S3	-0.044
S4	0.045
S5	-0.037
S6	0.037
Fe1	-0.534

(ii) Atoms defining plane: S1, S2, S5, S6

$$\text{Equation of plane } -0.3039X - 0.0461Y + 0.9561Z - 2.4151 = 0$$

<u>Atom</u>	<u>Deviation from Least Squares Plane (Å)</u>
S1	-0.114
S2	0.117
S5	-0.103
S6	0.100
Fe2	0.563

Table 11

Some Fe-S Distances in Dithiolene Complexes of Iron

Compound	Fe-S	Fe-S _{bridge}	S-Fe-S	Reference
$[\text{Fe}(\text{NO})\text{S}_4\text{C}_4(\text{CN})_4]^{2-}$	2.28	----		48
$\{\text{Ph}_3\text{POFe}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2\}^-$	2.23	----		49
$[\text{FeS}_4\text{C}_4(\text{CN})_4]_2^{2-}$	2.22	2.28	90.0	47
$\{\text{Fe}[\text{S}_2\text{C}_2(\text{CN})_2]_3\}^{2-}$	2.26	----	88.0	15
$[\text{Fe}(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)]_3$	2.21	2.23 2.34	87.1	This work.

Table 12

The 1, 2-Diphenyl - Dithiolene Ligand Geometry

S - C	C - C	C - C _{phen}	M - S - C	S - C - C	S - C - C _{phen}	C _{phen} - C - C	References
1.69	1.34	1.53	109	120	115	125	28,29
1.69	1.42	1.48	110	119	117	124	31,32
1.73	1.31	1.48	106	120	115	125	This work

Bond distances are in Angstroms, bond angles in degrees.

Fig. 2

A Perspective View of $\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)_3$

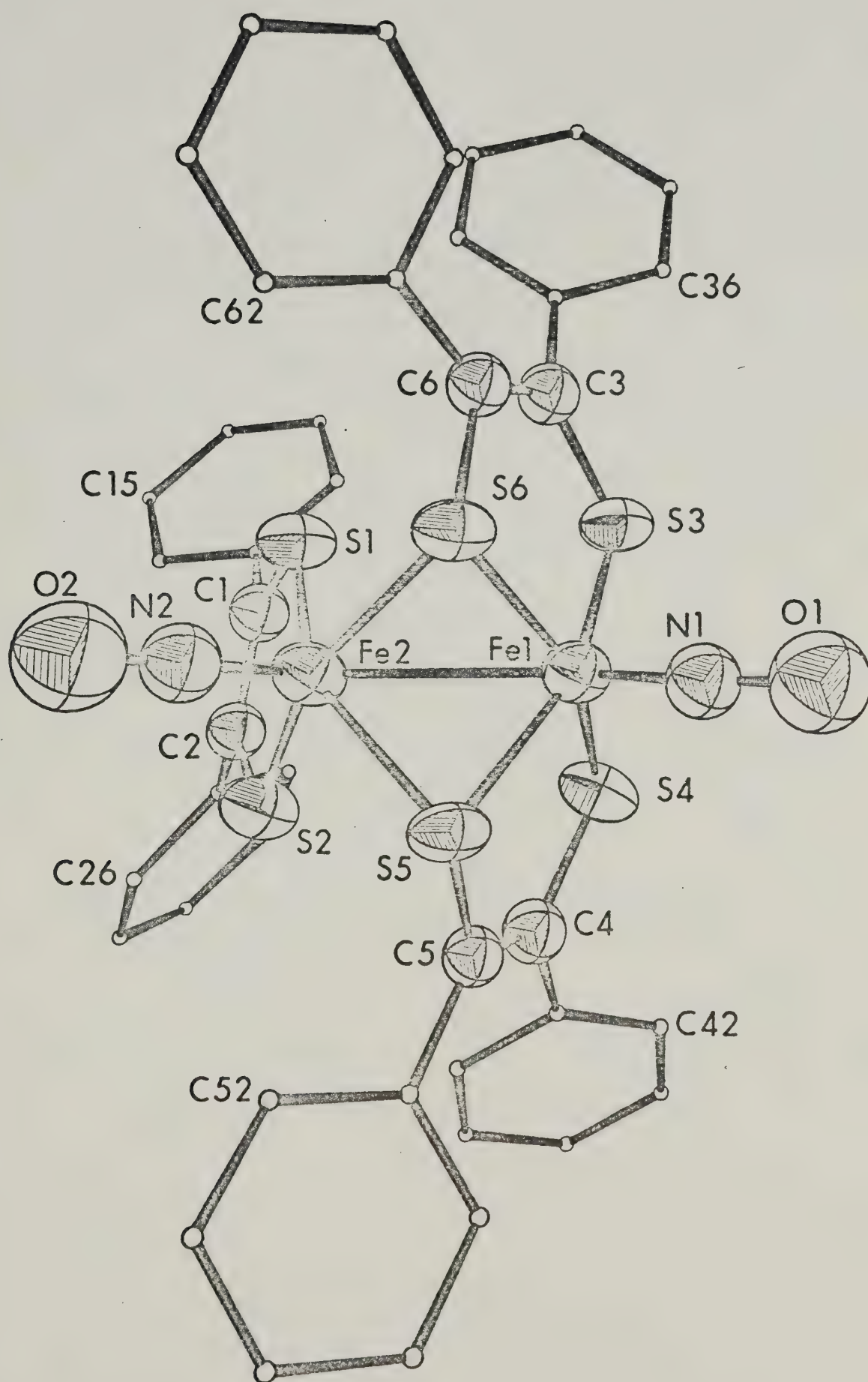
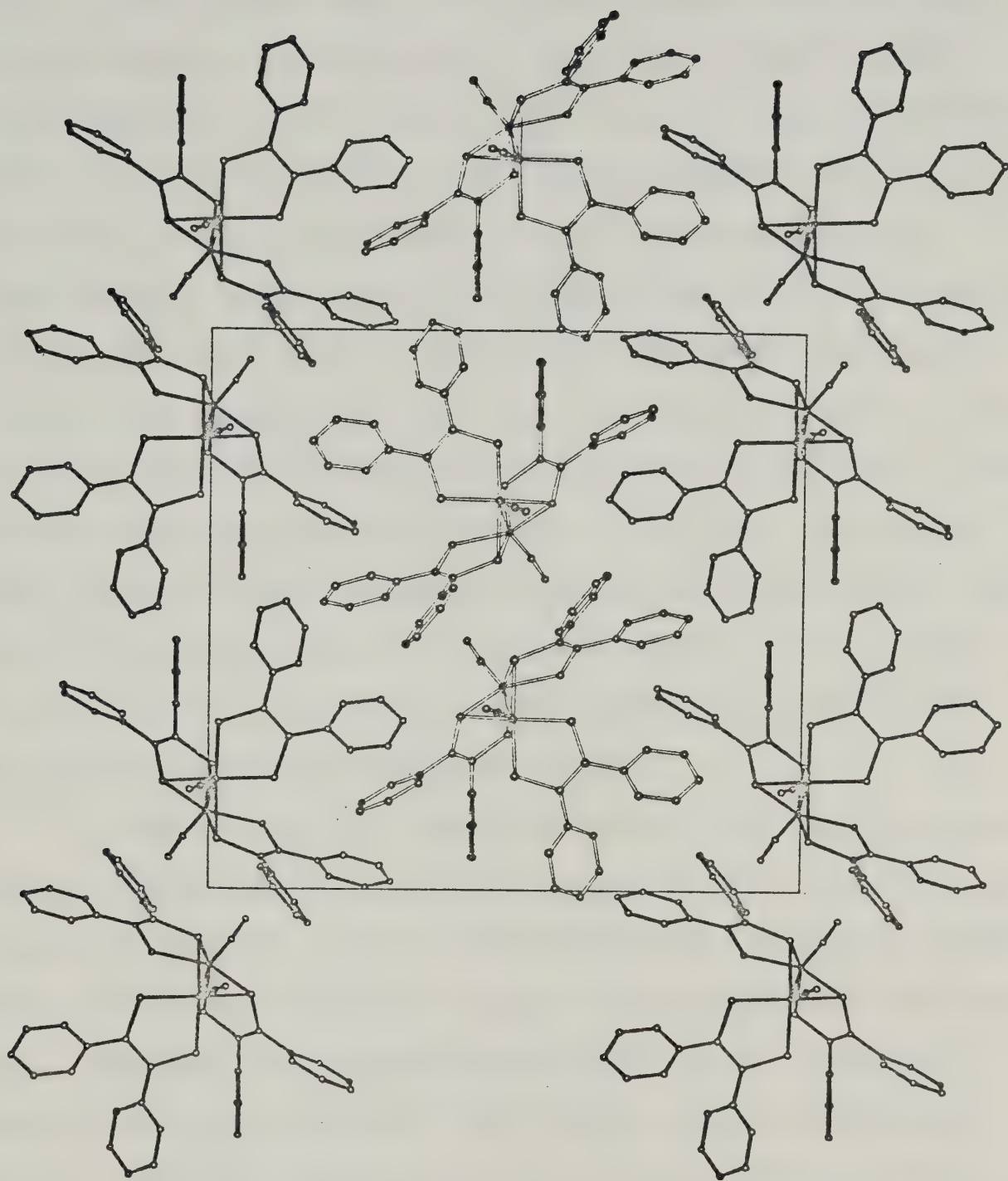


Fig. 3

Unit Cell Contents Projected on to [a][b] Plane



DISCUSSION

The geometry of the complex is shown in Fig. 2. The six sulphur atoms form a distorted trigonal prism. The distortion takes the form of the elongation of two sulphur-sulphur distances to 3.77 and 3.58 Å from the average distance of 3.08 Å found between the other sulphur atoms. Thus the prism has only two square faces, near the centre of which, sit iron atoms. Each iron atom is pentacoordinated, neglecting any iron-iron interaction, the coordination polyhedron being a square based pyramid in which the four sulphur atoms of the square face form the base and a nitrosyl group the apex. Both iron atoms are displaced 0.56 Å out of the plane containing the four sulphur atoms toward the apical nitrosyl group. An alternative description is to consider the two basal planes of the two square based pyramids as being joined along the S5-S6 line at a dihedral angle of 71.5°.

Despite the fact that both iron atoms have the same coordination polyhedron, the environment of each iron atom is distinctly different. One of the dithiolene ligands is coordinated only to Fe2, while the other two are formally attached to Fe1. However, one sulphur atom from each of these two ligands also forms a bond to Fe2, making these two ligands bridging. The bond to Fe2, however, is weaker than to Fe1, and this is reflected in the different iron-sulphur bond lengths in the bridging system. The average Fe1-S bridge bond length is 2.22 Å while the Fe2-S bridge bond length is 2.34 Å, signif-

icantly longer.

Although both metal ions are formally electron deficient, and this would be relieved to some extent by the formation of an iron-iron bond, the internuclear distance of $2.780 \text{ \AA}$ in this compound is toward the long end of the range of iron-iron bond distances that have been observed in various complexes, ranging from $2.43 \text{ \AA}$ in $\text{Fe}_3(\text{CO})_8(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2$ ⁴⁵ to $3.05 \text{ \AA}$ in $[\text{Fe}(\text{NO})_2\text{I}]_2$.⁴⁶ It remains, therefore, a valid question as to whether or not an iron-iron bond exists in this complex.

Dithiolene ligands acting as sulphur bridges between iron ions have also been observed in the anion $[\text{Fe}_2\text{S}_4\text{C}_4(\text{CN})_4]^{2-}$ whose structure was determined by Hamilton and Bernal.⁴⁷ In this anion it was postulated that there was no iron-iron bond, interaction between unpaired electrons in the Fe(III) ions taking place via the sulphur bridges. The iron-iron separation was $3.08 \text{ \AA}$ and Fe - S bridge - Fe angle was 81° .

Dahl et al have pointed out, that the Metal - Bridge - Metal angle is sensitive to the presence or absence of a metal-metal bond.⁴⁶ In complexes containing a metal-metal bond the angle tends to be quite acute, ranging from $68^\circ - 74^\circ$, whereas in the absence of a bond they are much larger, usually close to 90° . In this compound, the two Fe1 - S bridge - Fe2 angles average 75.1° which is very close to that of compounds in which there is a metal-metal bond.

It is concluded then, that the shortening of the iron-iron distance from the nonbonded contact of $3.08 \text{ \AA}$ in

$[\text{FeS}_4\text{C}_4(\text{CN})_4]_2^{2-}$ to $2.780 \text{ \AA}$, together with the contraction of the Fe - S bridge - Fe angle, is indicative of the presence of an iron-iron bond in this compound, albeit a weak one.

The two long sulphur-sulphur contacts between S2 and S4, and S1 and S3 must be considered as being due to repulsive interaction between these pairs of atoms. In the monomeric tris dithiolene complexes which have trigonal prismatic geometry, it has been suggested that interligand sulphur-sulphur bonding is a significant factor in stabilising the geometry^{28,29,31,35}. If the sulphur-sulphur interactions are attractive, then this compound could gain extra stability by formation of a trigonal prism of S atoms. If the S2 - S4 and S1 - S3 distances shortened to $3.1 \text{ \AA}$, the Fe - Fe distance would become $2.55 \text{ \AA}$ which would not be too short for an iron-iron bond. Also, there are no steric interactions between phenyl rings attached to C3 and C4 with those attached to C1 and C2, preventing the sulphur atoms from moving closer together. The closest approach of two atoms in the above entities is $3.43 \text{ \AA}$ between H12 and H32. It would appear, therefore, that interligand S - S bonding assumes its maximum importance only if there is a single metal cation at the centre of the trigonal prism.

There are two iron-sulphur bond distances in the complex. The iron-sulphur distances within the five-membered rings formed by the metal ion and the dithiolene ligands average $2.21 \text{ \AA}$ which is similar to that found in other di-

thiolene complexes of iron^{15, 47-49}. This information is summarised in Table 11. The iron-sulphur bonds in the chelate ring attached to Fe2 may be slightly shorter than in those attached to Fe1, indicating more Fe - S π -bonding in the Fe2 - S1 - S2 system, but differences of this magnitude cannot be distinguished with this data set. The other iron-sulphur distance is the Fe2 - S_{bridge} bond length, which is 2.34 Å and definitely longer than any of the other iron-sulphur bond lengths in the complex. This situation is similar to that found by Bernal and Hamilton⁴⁷ in $[\text{FeS}_4\text{C}_4(\text{CN})_4]^{2-}$, in which the Fe - S_{bridge} bond length is long to the sulphur atom which is part of the chelate ring attached to the other metal ion.

Thus the iron ions are not symmetrically bridged by the sulphur atoms, giving rise to two iron environments which agrees with the observation of two iron sites in the Mössbauer spectrum. The coordination of solvent is definitely not responsible for the difference between the two iron environments, as has been suggested elsewhere⁴⁰, since the closest approach of either of the two chlorine atoms to an iron atom is 6.52 Å.

If this structure were maintained in solution after reduction to the monoanion, it could explain the observation of the triplet signal in the E.S.R. spectrum since it is possible to envisage that the extra electron could be localised on one half of the dimer, probably on Fe1 since it is formally the most electron deficient. If this were the case, then the

electron could only interact with one ^{14}N nucleus, giving rise to a triplet signal. However, this would not explain the observation of one iron site in the Mössbauer spectrum of the monoanion¹⁴ and probably a separate crystal structure of the monoanion will be necessary to resolve this problem.

The average geometry of the 1,2-diphenyldithiolene ligand is similar to that which has been found in two other compounds in which it is present^{28,29,31,32}. This geometry is summarised in Table 12.

Also of interest is the mode of attachment of the nitrosyl group. The nitrosyl group has been found to co-ordinate in both linear and bent manner. These two different types of bonding have been regarded as being due to the amphoteric nature of NO^+ ⁵⁰. Compounds in which the NO^+ acts as a Lewis base, donating a pair of σ electrons to the metal using an sp hybrid on nitrogen, are characterised by $\text{M} - \text{N} - \text{O}$ angles of 180° and short metal-nitrogen bond lengths due to extensive π back-bonding from the metal to the NO moiety. Compounds in which the NO^+ acts as a Lewis acid, accepting electrons from the metal using an sp^2 hybrid orbital, have $\text{M} - \text{N} - \text{O}$ angles close to 120° and longer $\text{M} - \text{N}$ bond lengths.

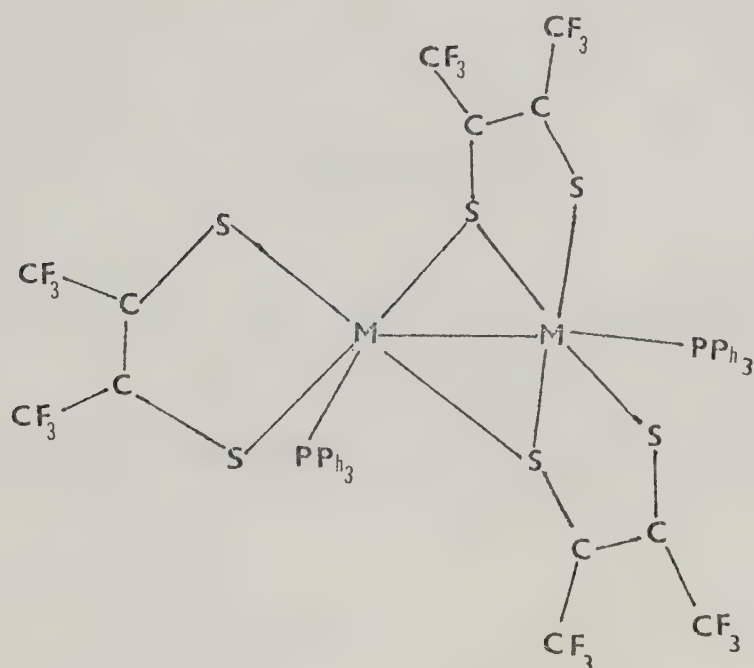
In $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)_3]$, neither $\text{Fe} - \text{N} - \text{O}$ angle differs significantly from 180° . The $\text{Fe} - \text{N}$ distances average $1.56 \text{ \AA}$ and the $\text{N} - \text{O}$ distance is $1.22 \text{ \AA}$. These distances are similar to others found for iron-nitrosyl bonds where the nitrosyl is attached in an essentially linear fashion^{48,51,52}.

Clearly in this compound there is significant π -bonding between the iron and the nitrosyl group.

At the time this structure was determined, no other compounds were known which possessed this type of bridging, in which two dithiolene ligands chelating the same metal ion form sulphur bridges to a second metal ion. Recently however, the structure of dicarbonyl bis (triphenyl phosphine) tris (toluene-3,4-dithiolate) diiridium(III) was published⁵³. This compound contains the same type of dithiolene bridging and the variation of bond lengths in the bridging unit is the same as in the iron dithiolene complex. The Ir - S distances from one iridium to the bridging sulphur atoms, which form part of the chelate systems attached to the other iridium atom, are longer than all other Ir - S bond lengths. There is no Ir - Ir bond in the compound and the Ir - S_{bridge} - Ir angle is 98.4°.

This type of bridging has also been postulated to explain the n.m.r. spectrum of Mo₂(tdt)₅ which indicates four distinct ligand environments⁵⁴. This type of bridging may also be present in the two compounds [M₂(PPh₃)₂(S₂C₂(CF₃)₂)₃] (M = Rh, Ir), prepared by McCleverty *et al*⁵⁵, since it would readily explain the ¹⁹F n.m.r. spectrum of these complexes. The spectrum consisted of two quartets (1 : 3 : 3 : 1) and a singlet. The relative areas of these signals are 1 : 1 : 1 which have been postulated as having arisen from three different pairs of CF₃ groups, two of which were mutually coupled. Two possibilities exist: either there are three chemically distinct

sulphur ligands in the compounds or the CF_3 groups are non-equivalent in two of them. If the latter were the case, then the structure 4 could be postulated, with bridging dithiolene ligands of the type found in $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)_3]$, making the CF_3 groups in these ligands nonequivalent. It is possible, therefore, that $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)_3]$ is only one of a family of compounds having this type of bridging system.

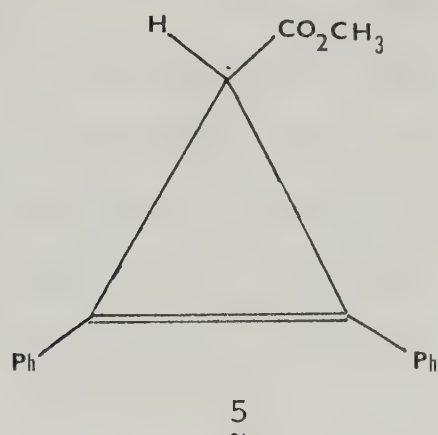


Chapter Two

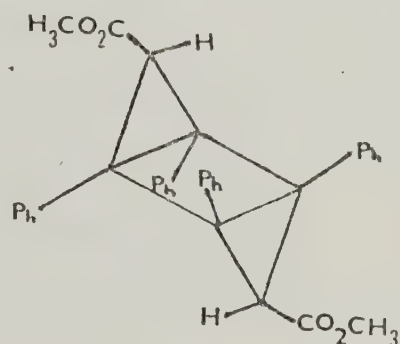
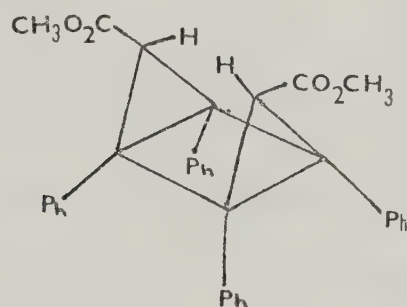
The Crystal and Molecular Structures of
1,2,4,5-tetraphenyl-
3,6-dicarbomethoxycyclohexa-1,4-diene.

INTRODUCTION

The photodimerisation of 3 carbomethoxy-1,2-diphenylcyclopropane **5** was carried out in this department by Dr. S. Masamune and S. Takada⁵⁶. Two products were obtained which



were tentatively assigned *cis*- and *trans*- tricyclic structures **6** and **7** on the basis of their n.m.r. and u.v. spectra. However, these physical data are not sufficient to distinguish between the four symmetrical tricyclo[3.1.0.0^{2,4}]hexane and two cyclohexa-1,4-diene structures which are possible for the



two photodimers. The X-ray crystal structure determinations of both compounds were undertaken to establish the stereochemistry of these compounds and to determine the exact geometry of the novel tricyclic systems. The crystal structure of the

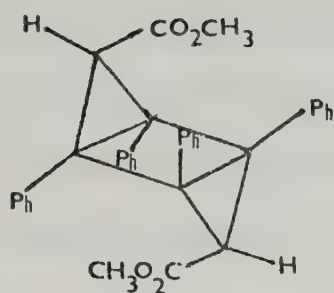
tricyclic compound 7 will be discussed in the next chapter.

Raman spectra of the two compounds in the region $1600 - 1700 \text{ cm}^{-1}$ indicated that the assignment of the tricyclic structures to 6 was incorrect. Both spectra exhibited intense peaks at 1600 cm^{-1} which could be attributed to the carbonyl group, while 6 showed an additional strong band at 1680 cm^{-1} , a value consistent with the $\text{C} = \text{C}$ ring stretching frequency of a cyclohexa-1,4-diene structure⁵⁷. The X-ray analysis of this compound was continued because the stereochemistry of the compound was still unestablished and also because the conformation of cyclohexa-1,4-diene itself has been the subject of some controversy.

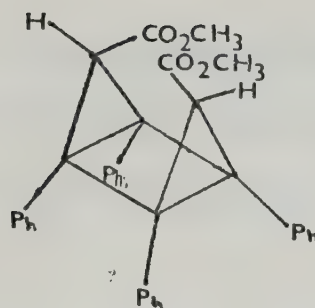
The photodimer may be either *syn*- or *anti*- 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene, if it is considered as being formed by the rearrangement of a tricyclic compound.



In addition to 6 and 7, two other compounds 8 and 9 could be formed in the photo dimerisation.



8



9

It can be seen then that 6 and 9 would rearrange to give the *syn* product while 7 and 8 would give the *anti*-cyclohexadiene derivative, assuming a photochemical mechanism.

The conformation of cyclohexa-1,4-diene has been studied by various methods. Gerding and Haak assigned the molecule a planar structure with D_{2h} symmetry on the basis of its vibrational Raman and infrared spectrum⁵⁸. Monsotori and Weber came to the same conclusion from rotational Raman data⁵⁹. The conclusions of Gerding and Haak were later confirmed by Stidham⁵⁷. A more recent study by R.C. Lord and J. Laane in the far infrared region also favored a planar structure⁶⁰. Although the results of these investigations indicate that the planar conformation may be the most stable, they are not conclusive and cannot rule out the possibility that small amounts of a boat form with C_{2v} symmetry is present, nor a form rapidly interconverting between C_{2v} and C_{2h} (chair form) symmetry through the planar D_{2h} symmetry⁵⁷.

1,4-Dichlorocyclohexa-1,4-diene has been found to have a measurable dipole moment of 0.3 D.U., indicating that in this compound at least the cyclohexa-1,4-diene ring is non-

planar⁶¹. Dipole moment measurements on cyclohexadiene itself suggested a small dipole moment, but the experimental error was too large to distinguish between the planar and boat conformations⁶².

Herbstein concluded, from calculations in which the angle strain and steric interaction between hydrogens was minimised, that the boat form was the most stable conformation, and that the dihedral angle between the two halves was approximately 140° ⁶³. However, Favini *et al*, taking a similar approach, but introducing an extra factor, due to torsional strain from rotation around single bonds, found that the planar conformation was the most stable⁶⁴.

Two electron diffraction studies of cyclohexa-1,4-diene have been carried out^{65,66}. Dallinga and Toneman⁶⁵ considered chair, boat, planar and skew conformations in the initial stages of their refinement, but since the refinement of the boat, skew and chair models did not converge, only the planar model was pursued to completion. The conclusion they drew from their calculations was that the molecule was essentially planar but that other conformations, especially the chair form, could not be precluded with certainty. However, the suggested deviations from the plane were $\leq 0.05 \text{ \AA}$.

On the other hand, Oberhammer and Bauer⁶⁶, obtained a structure with a boat conformation. The dihedral angle between the two halves of the molecule was 159.3° corresponding to a deviation of $0.23 \text{ \AA}$ from the diene plane for the methylene

type carbon atoms.

Crystal structure determinations to date have not been very helpful in resolving the problem. The crystal structures of 1,4-dicarbomethoxycyclohexa-1,4-diene has been determined in two forms^{67,68}. The molecule was found to be planar, but due to the poor quality of the data, small deviations from planarity would not have been detected. However, since the molecule occupies an inversion centre in the unit cell, it is definitely not in the boat conformation, unless disordered. The structure of 1,4-cyclohexadiene-1-glycine was also found to be planar within experimental error⁶⁹, but again, small deviations from planarity to either the boat or chair form could not be detected.

In view of the contradictory conclusions arrived at regarding the structure of the cyclohexa-1,4-diene ring, the X-ray crystal structure determination of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene was undertaken in order to provide additional evidence concerning the planarity of this ring system.

EXPERIMENTAL

1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene crystallises as transparent needles. A suitable crystal was chosen and examined by photographic methods (dimensions 0.15 mm x 0.07 mm x 0.07 mm). Weissenberg photographs for the $h0\ell$, $h1\ell$ and $h2\ell$ layers were obtained together with precession photographs for the $0k\ell$ and $hk0$ layers. The Laue symmetry was found to be $2/m$ and the crystals to be monoclinic. The following systematic absences:

- (i) $hk\ell$ $h + k + \ell = 2n + 1$ implying a body centered cell
- (ii) $h0\ell$ $h = 2n + 1$ implying an a glide perpendicular to b.

defined the space group as either $I2/a$ which is centrosymmetric or Ia which is non-centrosymmetric.

The lattice parameters were obtained by the least squares refinement of the 2θ values for several high angle reflections, these having been accurately measured using a PICKER manual four circle diffractometer. The results obtained were: $a = 20.052(1)$; $b = 5.756(1)$; $c = 22.782(2)$; and $\beta = 95.73^\circ(1)$.

The density obtained experimentally by flotation in aqueous potassium iodide solution was 1.26 gm cm^{-3} , while the calculated density for four molecules of molecular weight 400 in a cell of volume $2616.24 \text{ \AA}^3$ was 1.27 gms cm^{-3} . The density therefore requires that the molecule occupies a special position, either on the two-fold axis or on a centre of symmetry, if the space group is $I2/a$, while there are no restrict-

ions if the space group is Ia.

Intensity data were collected on a PICKER manual diffractometer using graphite crystal monochromated $\text{CuK}\alpha$ radiation, the crystal being mounted with the b axis along the ϕ axis of the diffractometer. The intensity data were collected using the coupled $\omega/2\theta$ scanning technique. The scan width was 2° with a scan rate of $2^\circ/\text{min}$. and a 2θ maximum of 120° . A stationary background count was taken for 30 seconds on each side of the scan.

Before the data collection was complete, the crystal was inadvertently lost, and it was necessary to complete the intensity measurements with a second crystal. The intensities of six reflections were measured periodically throughout the data collection and with neither crystal was there any evidence of decomposition taking place.

During the data reduction process, reflections were rejected if $I \leq 0$ or if $I \leq 3\sigma$. Of the 1940 reflections collected 875 were rejected in this way, giving 1065 observed reflections.

An absorption correction was not applied, the linear absorption coefficient for this compound being only 6.67 cm^{-1} . The data were corrected for Lorentz and polarisation effects and structure factor amplitudes and standard deviations calculated, using an uncertainty factor⁷⁰ p of 0.03.

SOLUTION OF STRUCTURE AND REFINEMENT

The structure was solved by direct methods using the programmes FAME and MAGIC, to produce E statistics and to carry out the symbolic addition procedure, respectively. Since MAGIC was not programmed to carry out the symbolic addition procedure for a body centred cell, it was necessary first of all to transform the indices of the reflections to those of an A centred cell which had common [a] and [b] axes. This was accomplished by means of the following transformation matrix:

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix}_A = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix}_I$$

The cell parameters for the A centred cell were $a = 20.052$; $b = 5.756$; $c = 31.818$; $\beta = 134.568$. This cell was not used in the subsequent refinement because of the very large β angle.

Normalised structure factors were calculated, using the method described on page 20. The distribution of the normalised structure factors is dependent upon whether or not the space group is centrosymmetric. The distribution obtained is shown below and compared with the theoretical values.

The distribution for this structure is in very close agreement with the theoretical distribution for a centrosymmetric space group and from this point on the space group I2/a (A2/a for FAME and MAGIC) was assumed to be the correct

	This Structure	Centro- symmetric	Non-centro- symmetric
$\langle E \rangle$	0.820	0.798	0.886
$\langle E ^2 \rangle$	0.988	1.000	1.000
$\langle E ^2 - 1 \rangle$	0.958	0.968	0.736
Percentage $ E > 1$	28.45	32.00	37.00
Percentage $ E > 2$	4.77	5.00	1.80
Percentage $ E > 3$	0.39	0.30	0.01

one.

Woolfson has pointed out that the greatest weakness of the symbolic addition method is in the early stages of its application, when single sign relationships must be relied upon to determine new signs⁷¹. For this reason, the initial input to the symbolic addition programme MAGIC consisted only of those reflections with very high E values (greater than 2.0), since any relationships between these will lead to new signs which have a high probability of being correct.

The following seven reflections which were of large $|E|$ were assigned symbols and used to initiate the symbolic addition procedure:

I2/a			A2/a			E	Symbol
-9	2	13	-9	2	22	3.127	A
4	1	19	4	1	15	2.709	B
-9	3	12	-9	3	21	4.046	C
14	2	6	14	2	-8	3.014	D
17	2	5	17	2	-12	2.668	E
2	1	19	2	1	17	3.700	F
-3	5	2	-3	5	5	3.244	G

A new phase was not accepted if the probability of it being correct was below 0.990. After several new phases had been determined, this criterion was relaxed slightly but the acceptance level was not allowed to drop below 0.987. Twenty-two new signs were determined bringing the total to 29. These were used as input to MAGIC using the full set of data with $|E| > 1.500$. The probability acceptance level was set initially at 0.990 and allowed to fall slowly as the sign determination proceeded to 0.982. 133 more signs were determined giving a total of 162 phases determined in terms of the seven starting symbols.

Throughout the determination, relationships between the symbols became apparent. For example, if a sign was determined as +A with a probability of 0.9 and also as +B with a probability of 0.8, then there is an indication that AB is positive with a probability of 0.72. These relation-

ships, are summarised below:

Symbol	Number of indications of + with probability ≥ 0.90	Number of indications of - with probability ≥ 0.90
1. CEF	3	0
2. CDG	1	0
3. BF	2	2
4. BCDFG	0	3
5. ADFG	1	87
6. ACF	0	2
7. ACDEG	0	17
8. ABDG	4	2

It was obvious that only relationships 5, ADFG = -, and 7, ACDEG = -, could be used with any confidence to reduce the number of possible solutions to a manageable number. Reflections -9 2 22 and -9 3 21 (A2/a) were used to determine the origin, both being given + signs. This, of course, made symbols A and C both positive, so that relationships 5. and 7. reduced to DFG = - and DEG = -. Therefore, F and E were of the same sign. B remained unknown. Using the above relationships between D, F and G and placing no restrictions on B, a total of eight possible solutions was obtained. These are given in the table below:

Solution Number	A	B	C	D	E	F	G
1.	+	+	+	-	+	+	+
2.	+	+	+	+	+	+	-
3.	+	-	+	-	+	+	+
4.	+	-	+	+	+	+	-
5.	+	+	+	+	-	-	+
6.	+	+	+	-	-	-	-
7.	+	-	+	+	-	-	+
8.	+	-	+	-	-	-	-

From the less certain relationship $BCDFG = -$, $B = +$ was obtained, and so the three dimensional E maps (Fourier maps in which the E's whose phases had been determined were used as coefficients) for solutions 1, 2, 5 and 6 were computed first.

In the E map corresponding to solution 2. i.e. $A = B = C = D = F = +$, $G = -$, a six-membered ring occupying a centre of symmetry at the cell origin was easily detected.

Further inspection of this map revealed the positions of all the nineteen carbon and oxygen atoms in the asymmetric unit. The coordinates of these atoms were used to compute structure factors using scattering factors for carbon and oxygen calculated from Cromer's coefficients. A residual R

factor of 0.273 was obtained which reduced to 0.097 after three cycles of full matrix least squares refinement.

An electron density difference map computed at this point in the refinement revealed the positions of all the hydrogen atoms in the asymmetric unit apart from the three methyl hydrogens.

These eleven hydrogen atoms were now included in the structure factor calculations and least squares refinement, their contribution to the overall scattering being calculated from the scattering factors of Mason and Robertson⁴³. Two cycles of refinement reduced the R factor to 0.082, but the positions of the hydrogen atoms of the methyl group were not resolved in a difference Fourier calculated from this data. The difference Fourier was recalculated using only the data with $\sin \theta/\lambda \leq 0.35$, since this data is more sensitive to the light atom positions than the high order reflections because the scattering power of the light atoms falls off more rapidly than that of heavier atoms as $\sin \theta/\lambda$ increases and the high angle data are particularly sensitive to errors in thermal parameters. From the resulting difference map the positions of the three hydrogens were located and included in all remaining structure factor calculations and least squares refinement cycles.

In two more cycles of full matrix least squares refinement the R factor fell to 0.070 and an electron density difference map calculated at this point gave evidence of

anisotropic thermal motion for many of the carbon and oxygen atoms. Consequently, the carbon and oxygen atoms were allowed to refine anisotropically and in four more cycles the R factor converged at 0.043.

Inspection was then made of the observed and calculated structure amplitudes, where it was seen that the observed structure amplitudes with low $\sin \theta/\lambda$ and relatively large magnitude were consistently smaller than the calculated structure factors, indicating that the crystals suffered from secondary extinction and that a correction was necessary. The calculated structure factors were modified by the term $1/(1 + \beta(2\theta))$. C.I.) suggested by Zachariasen⁷². I was the raw intensity, C was the secondary extinction parameter, which became a variable parameter in the subsequent refinement, and $\beta(2\theta)$ accounts for the angular variation of the extinction correction. This latter term could be split into two components, a polarisation term and an absorption term.

$$\beta(2\theta) = \frac{(1 + \cos^2 2\theta_m)(\cos^2 2\theta_m + \cos^4 2\theta)}{(\cos^2 2\theta_m - \cos^2 2\theta)^2} \times \frac{A^*(2\theta)}{A^*(0)}$$

where $2\theta_m$ was the monochromator angle. The second term was a ratio of absorption factors at 2θ and at $2\theta = 0$. Since absorption was negligible in this crystal, this ratio was assumed to be 1 and the calculated structure factors were corrected for the polarisation part of the extinction correction only.

When this correction was applied, the refinement

converged in two cycles to $R_1 = 0.040$ and $R_2 = 0.042$. The largest peak in an electron density difference map, computed at the end of the refinement, was 0.17 electrons per $\text{\AA}^3$.

Of the 162 phases determined with the Σ_2 relationship, only four were incorrect, and these all occurred in the later stages of the sign determination.

RESULTS

The observed ($|F_o|$) and calculated ($|F_c|$) structure amplitudes (electrons $\times 10$) are listed in Table 13. The final atomic coordinates for all atoms and isotropic temperature factors for the hydrogen atoms are given in Table 14, the anisotropic temperature factors for the carbon and oxygen atoms are listed in Table 15. Interatomic distances and angles are listed in Tables 16 and 17.

A diagram of the molecule is shown in Fig. 4, and a packing diagram with the molecules projected on to the $[a][c]$ plane is shown in Fig. 5. Some selected views of the molecule along certain bonds are given in Fig. 6.

Table 13

Observed and Calculated Structure Amplitudes (electrons $\times 10$)

H	L	FORM	PCAL	H	L	FORM	PCAL	H	L	FORM	PCAL	H	L	FORM	PCAL	
K = 0**																
-22	4	340	313	4	22	182	173	-11	2	140	151	0	21	157	141	
-22	6	349	341	6	0	280	284	-11	4	256	247	0	25	171	195	
-20	4	421	411	6	0	775	784	-11	6	124	114	1	0	301	324	
-20	6	531	529	6	2	1196	1144	-11	8	714	714	1	2	1101	1119	
-20	8	129	124	6	4	139	154	-11	10	154	163	1	4	95	79	
-20	10	173	173	6	6	1364	1313	-11	12	171	133	1	6	349	353	
-18	6	113	76	6	8	1753	1671	-11	14	177	196	1	8	473	441	
-18	8	350	359	6	10	457	461	-11	16	106	117	1	10	99	75	
-18	12	182	189	6	12	429	481	-10	1	209	194	1	14	389	381	
-16	4	155	148	6	14	324	303	-10	3	302	282	1	16	127	113	
-16	6	237	232	6	20	384	369	-10	5	110	98	1	18	265	259	
-16	8	359	345	6	22	302	326	-10	7	104	93	1	20	449	441	
-16	10	129	131	8	0	490	482	-10	9	324	316	1	22	111	132	
-16	12	293	302	8	2	730	722	-10	11	149	155	2	1	784	824	
-16	14	114	85	8	4	209	208	-10	13	253	277	2	3	249	240	
-16	16	186	190	8	6	543	509	-9	2	311	313	2	5	439	455	
-14	2	401	395	8	8	468	474	-9	4	536	537	2	7	645	649	
-14	4	176	194	8	10	299	284	-9	6	449	450	2	9	469	472	
-14	6	319	341	8	12	264	279	-9	8	244	230	2	11	215	202	
-14	8	348	335	8	14	382	375	-9	10	288	286	2	13	612	604	
-14	10	141	137	8	16	234	267	-9	12	360	358	2	15	203	206	
-14	12	624	620	8	18	581	591	-9	14	235	278	2	17	158	165	
-14	14	541	539	10	0	136	118	-9	16	153	166	3	19	254	264	
-14	16	271	285	10	2	55	89	-9	18	104	105	3	21	778	816	
-12	2	232	218	10	4	463	449	-8	20	928	951	3	23	1745	1740	
-12	4	116	121	10	6	249	236	-8	22	870	879	3	25	723	733	
-12	6	672	652	10	8	524	493	-8	24	531	513	3	27	341	358	
-12	8	458	458	10	10	217	219	-8	26	131	138	3	29	180	168	
-12	10	216	209	10	12	177	161	-8	28	118	115	3	31	213	215	
-12	12	266	221	10	14	206	208	-8	30	116	92	3	33	233	231	
-12	14	337	355	12	0	268	293	-8	32	155	170	3	35	171	154	
-12	16	130	134	12	2	123	115	-8	34	114	125	4	1	1141	1153	
-10	2	147	171	12	4	565	523	-8	36	148	178	4	3	889	914	
-10	4	57	106	12	6	201	212	-8	38	133	116	4	5	189	190	
-10	6	299	298	12	8	142	120	-7	40	816	829	4	7	192	172	
-10	8	592	576	12	10	140	141	-7	42	237	234	4	9	480	466	
-10	10	137	155	12	12	143	137	-7	44	417	428	4	11	292	288	
-10	12	516	529	12	14	134	134	-7	46	838	856	4	13	171	170	
-10	14	336	348	12	16	169	185	-7	48	375	376	4	15	486	479	
-10	16	182	200	14	0	413	400	-7	50	292	287	4	17	493	501	
-8	2	105	111	14	2	267	197	-7	52	210	200	4	19	418	407	
-8	4	636	639	14	4	225	250	-7	54	132	138	4	21	166	175	
-8	6	96	82	14	6	368	334	-7	56	160	195	5	1	498	517	
-8	8	400	395	14	8	97	97	-7	58	185	189	5	3	1439	1460	
-8	10	812	805	14	10	247	248	-7	60	127	108	5	5	382	380	
-8	12	210	219	16	0	325	305	-6	62	132	131	5	7	203	208	
-8	14	222	223	16	2	158	314	-6	64	285	298	5	9	360	354	
-8	16	126	140	16	4	142	110	-6	66	265	268	5	11	349	342	
-6	2	695	700	16	6	273	268	-6	68	412	441	5	13	825	802	
-6	4	1186	1181	16	8	240	246	-6	70	596	593	5	15	136	131	
-6	6	668	668	16	10	144	177	-6	72	298	289	5	17	363	352	
-6	8	342	341	16	12	371	368	-6	74	366	357	5	19	222	223	
-6	10	720	698	16	14	335	326	-6	76	15	124	110	5	21	339	331
-6	12	355	349	16	16	467	440	-6	78	127	242	5	23	190	181	
-6	14	430	422	18	0	134	137	-5	80	252	987	6	1	757	777	
-6	16	185	169	18	2	210	213	-5	82	642	674	6	3	403	401	
-6	18	341	340	20	4	267	247	-5	84	559	1000	6	5	458	461	
-4	2	2107	2149	20	6	237	223	-5	86	318	318	6	7	529	524	
-4	4	1703	1707	20	8	118	190	-5	88	276	254	6	9	583	550	
-4	6	253	266	20	10	230	247	-5	90	278	265	6	11	257	242	
-4	8	909	919	20	12	111	105	-5	92	155	145	6	13	329	330	
-4	10	1511	1472	20	14	399	421	-5	94	179	176	6	15	176	185	
-4	12	555	543	20	16	751	785	-5	96	201	176	6	17	97	112	
-4	14	123	112	20	18	741	756	-4	98	251	213	7	19	192	199	
-4	16	123	141	20	20	5	933	-4	100	956	956	7	21	957	962	
-4	18	252	227	20	22	149	129	-4	102	184	184	7	23	681	675	
-4	20	292	302	20	24	119	114	-4	104	183	183	7	25	292	287	
-2	2	280	287	20	26	183	132	-4	106	177	177	7	27	231	251	
-2	4	1530	1546	20	28	129	138	-4	108	287	206	7	29	297	302	
-2	6	206	205	20	30	202	184	-4	110	157	144	7	31	157	144	
-2	8	1064	1060	20	32	359	370	-3	112	109	76	7	33	109	76	
-2	10	215	208	20	34	457	457	-3	114	157	155	8	1	157	155	
-2	12	203	193	20	36	1012	1024	-3	116	387	410	8	3	387	410	
-2	14	381	389	20	38	409	408	-3	118	580	857	8	5	880	857	
-2	16	113	101	20	40	528	502	-3	120	167	183	8	7	167	183	
0	2	875	889	20	42	170	161	-3	122	180	174	8	9	180	174	
0	4	337	341	20	44	339	346	-3	124	204	221	8	11	204	221	
0	6	814	826	20	46	255	261	-3	126	183	179	8	13	183	179	
0	8	269	262	20	48	1020	1061	-3	128	421	408	9	1	421	408	
0	10	201	175	20	50	666	668	-3	130	453	463	9	3	453	463	
0	12	315	302	20	52	560	539	-3	132	560	539	9	5	560	539	
0	14	210	212	20	54	306	290	-3	134	306	290	9	7	306	290	
0	16	262	273	20	56	185	207	-3	136	185	207	9	9	185	207	
0	18	389	390	20	58	213	220	-3	138	213	220	9	11	213	220	
0	20	1150	1163	20	60	311	334	-3	140	311	334	9	13	311	334	
0	22	146	147	20	62	334	336	-3	142	334	336	9	15	334	336	
0	24	660	653	20	64	119	156	-3	144	119	156	9	17	119	156	
0	26	1585	1623	20	66	481	491	-3	146	481	491	9	19	481	491	
0	28	1306	1313	20	68	141	141	-3	148	141	141	9	21	141	141	
0	30	744	742	20	70	167	165	-3	150	167	165	9	23	167	165	
0	32	148	140	20	72	365	374	-3	152	365	374	9	25	365	374	
0	34	435	426	20	74	807	793	-3	154	807	793	9	27	807	793	
0	36	263	274	20	76	314	319	-3	156	314	319	9	29	314	319	
0	38	970	952	20	78	303	294	-3	158	303	294	9	31	303	294	
0	40	274	251	20	80	230	240	-3	160	230	240	9	33	230	240	
0	42	276	259	20	82	196	207	-3	162	196	207	9	35	196	207	
0	44	1381	1411	20	84	174	159	-3	164	174	159	9	37	174	159	
0	46	966	975	20	86	502	487	-3	166	502	487	9	39	502	487	
0	48	2915	2935	20	88	5205	5205	-3	168	5205	5205	9	41	5205	5205	
0	50	595	624	20												

P	L	FOUR	FOUR	H	L	FOUR	FOUR	H	L	FOUR	FOUR	H	L	FOUR	FOUR	H	L	FOUR	FOUR
-5	3	364	357	8	4	184	364	-4	19	213	217	-16	4	241	254	9	7	161	177
-5	9	709	710	8	6	169	155	-3	4	501	483	-16	10	203	204	10	2	271	277
-5	13	249	250	8	8	316	319	-3	8	358	371	-15	5	244	245	10	4	104	101
-5	17	242	245	8	10	240	241	-3	14	353	354	-13	7	172	182	10	12	166	187
-5	19	251	241	8	12	343	345	-3	16	158	162	-12	8	287	312	11	5	161	151
-5	23	174	166	8	16	124	106	-3	18	245	265	-12	10	195	182	11	7	232	265
-4	2	454	466	9	1	278	276	-2	1	350	372	-12	12	115	116	12	6	255	240
-4	4	129	122	9	5	654	649	-2	3	184	183	-12	14	365	374	13	3	161	198
-4	6	115	130	9	7	119	89	-2	5	289	265	-11	1	217	204	14	0	326	345
-4	8	186	184	9	9	234	234	-2	9	134	117	-11	3	272	277	14	2	174	165
-4	12	342	332	9	11	152	170	-2	15	147	133	-11	5	122	122	14	6	322	340
-4	14	266	258	9	17	252	267	-2	21	111	105	-11	11	183	177	14	8	109	153
-4	16	152	142	10	0	334	335	-1	2	285	287	-11	13	250	262	15	7	249	231
-4	18	294	294	10	4	200	189	-1	4	373	357	-10	2	136	106	16	4	320	303
-4	20	291	288	10	6	698	706	-1	6	552	542	-10	4	402	387	16	6	183	127
-3	3	1424	1415	10	10	257	310	-1	8	228	231	-10	12	292	317	17	1	165	175
-3	5	433	451	10	14	386	412	-1	10	267	254	-9	7	270	285	17	3	221	235
-3	9	552	555	10	16	147	103	-1	18	195	188	-9	11	332	341	**K = 5****			
-3	11	341	345	11	3	400	403	0	1	526	515	-9	13	165	145	-14	3	130	147
-3	15	254	277	11	7	340	370	0	3	597	582	-9	17	117	84	-13	6	135	127
-3	17	233	223	11	13	233	235	0	7	278	250	-8	6	291	305	-12	5	137	157
-3	21	156	148	11	17	120	157	0	11	200	171	-8	8	157	167	-11	6	129	125
-2	2	739	747	12	2	294	280	0	15	243	239	-8	14	284	293	-10	5	160	169
-2	4	111	125	12	4	172	237	0	17	347	343	-7	3	142	117	-9	6	151	147
-2	6	303	302	12	8	299	318	0	19	188	187	-7	9	167	166	-8	9	187	196
-2	10	392	397	12	10	189	185	0	21	128	124	-6	4	164	134	-7	2	158	156
-2	12	267	275	12	12	230	248	1	0	355	364	-6	8	348	341	-7	8	135	150
-2	14	146	111	12	16	117	123	1	4	130	123	-6	10	128	124	-7	10	239	254
-2	18	366	361	13	3	316	317	1	8	167	163	-6	12	245	251	-6	3	157	135
-2	22	107	84	13	5	157	151	1	10	129	130	-6	16	215	200	-6	9	228	227
-1	1	208	223	13	7	238	246	1	12	173	182	-5	1	280	261	-5	6	154	165
-1	3	273	257	13	9	364	370	1	18	151	127	-5	3	277	274	-5	8	149	150
-1	7	172	166	14	0	206	205	1	20	189	187	-5	5	241	241	-5	12	276	266
-1	9	828	818	14	4	790	777	1	22	132	152	-5	7	276	289	-4	3	145	135
-1	11	313	321	14	6	586	583	2	1	676	651	-5	9	133	125	-4	7	132	137
-1	13	154	150	15	7	183	182	2	3	299	298	-5	13	308	284	-4	9	266	263
-1	17	441	449	16	2	158	172	2	5	584	538	-5	15	121	140	-4	11	139	158
-1	19	249	234	16	4	312	313	2	17	415	431	-4	2	242	256	-3	2	663	647
-1	23	120	103	16	14	120	134	2	21	135	107	-4	4	314	326	-3	8	255	262
0	0	104	99	17	5	421	417	3	0	297	279	-4	6	346	362	-2	1	393	396
0	2	537	534	17	7	138	156	3	2	211	218	-4	10	292	290	-2	3	431	433
0	4	784	780	18	0	123	136	3	4	333	323	-4	14	332	336	-2	7	188	197
0	6	451	446	18	2	134	94	3	6	595	571	-3	1	391	411	-2	9	205	198
0	8	465	461	18	6	150	215	3	8	133	116	-3	3	213	201	-1	6	311	202
0	12	205	205	18	10	205	193	3	10	210	192	-3	7	251	292	-1	8	273	269
0	14	216	209	**K = 3****				4	3	174	191	-3	11	134	118	-1	10	230	245
0	18	515	510	-18	7	108	94	4	5	142	155	-3	13	154	166	-1	16	186	186
0	20	129	145	-18	11	118	122	4	7	118	127	-3	15	150	153	0	1	220	217
1	3	252	231	-17	10	185	165	4	11	192	168	-3	17	128	154	0	3	250	266
1	5	140	131	-17	12	161	175	4	15	159	146	-2	2	394	384	0	5	228	213
1	7	417	427	-16	3	196	181	4	17	309	312	-2	4	346	327	0	7	124	101
1	9	250	250	-16	5	234	244	5	0	483	465	-2	8	176	157	1	0	457	437
1	11	163	173	-16	13	158	152	6	1	475	441	-2	14	191	181	1	4	151	152
1	13	294	287	-15	4	351	366	6	3	220	207	-2	18	168	164	1	6	218	216
1	17	268	250	-15	6	164	154	6	7	389	383	-2	20	232	250	2	1	201	200
1	23	147	180	-15	10	198	189	6	11	240	248	-1	5	140	153	2	3	165	178
2	0	914	921	-15	14	262	248	6	13	217	217	-1	9	131	126	2	15	166	179
2	2	603	571	-14	7	142	143	6	15	189	189	-1	11	253	246	3	0	492	483
2	4	158	156	-14	11	125	106	7	0	215	200	-1	17	157	208	3	6	225	232
2	6	628	605	-14	15	259	270	7	4	164	160	0	2	157	170	3	8	230	218
2	12	225	218	-13	2	276	247	7	6	152	131	0	4	438	445	3	10	144	132
2	14	310	305	-13	8	189	190	7	8	275	300	0	6	376	343	3	14	168	177
2	18	226	232	-13	14	394	429	7	10	212	179	0	12	161	169	4	1	225	227
2	20	237	229	-13	16	290	283	7	12	175	160	0	16	214	196	4	3	129	134
2	22	132	96	-12	13	412	430	7	14	218	219	1	3	279	268	4	7	148	155
3	1	428	432	-12	15	164	173	7	16	277	287	1	5	138	163	4	11	172	171
3	3	211	210	-12	17	340	346	8	7	419	431	1	7	135	120	4	15	175	175
3	5	551	557	-11	4	425	439	8	9	259	247	1	13	125	125	5	0	127	116
3	7	199	196	-11	6	224	248	8	11	323	307	1	15	117	107	5	4	157	139
3	9	374	366	-11	8	238	249	8	13	161	137	1	19	301	315	5	6	160	165
3	13	156	194	-11	12	455	455	8	15	163	148	2	2	164	165	5	8	210	203
3	15	158	189	-11	14	118	99	9	4	365	364	2	4	257	249	5	12	110	103
3	17	301	302	-10	1	196	193	9	10	226	213	2	6	320	311	6	1	167	175
3	19	114	101	-10	11	571	566	9	12	252	252	2	10	283	270	6	3	173	184
4	0	656	712	-10	13	367	308	9	14	143	145	2	12	240	234	6	7	246	264
4	2	452	451	-9	2	150	136	9	16	180	179	2	14	258	311	7	4	154	168
4	4	117	125	-9	6	258	279	10	7	330	332	2	16	402	416	7	6	201	206
4	6	407	404	-9	12	890	891	10	9	146	167	2	18	154	203	8	3	161	157
4	8	433	425	-9	16	210	199	10	11	221	222	3	1	196	185	8	7	135	142
4	16	399	388	-9	18	292	291	10	13	369	365	3	3	175	192	9	2	136	136
4	18	305	315	-8	1	294	272	11	0	231	198	3	13	142	137	9	4	138	122
4	20	138	135	-9	3	160	146	11	2	143	130	3	15	217	232	9	6	308	396
4	22	118	119	-8															

Table 14

Atomic Coordinates and Isotropic Temperature Factors

Atom	x	y	z	B
C1	0.0489 (2)	-0.0090 (6)	0.0510 (1)	2.22*
C2	-0.0143 (2)	0.0307 (6)	0.0604 (1)	2.29*
C3	-0.0706 (2)	0.0377 (7)	0.0104 (1)	2.31*
C4	-0.1180 (2)	-0.1633 (8)	0.0220 (1)	2.78*
C5	-0.2113 (3)	-0.2643 (13)	0.0726 (3)	5.83*
C11	0.1057 (2)	-0.0239 (6)	0.0990 (1)	2.31*
C12	0.1169 (2)	0.1543 (7)	0.1403 (2)	2.89*
C13	0.1707 (2)	0.1402 (8)	0.1845 (2)	3.57*
C14	0.2132 (2)	-0.0475 (8)	0.1871 (2)	3.77*
C15	0.2022 (2)	-0.2249 (8)	0.1461 (2)	3.81*
C16	0.1488 (2)	-0.2129 (7)	0.1021 (2)	3.28*
C21	-0.0383 (2)	0.0590 (7)	0.1204 (1)	2.35*
C22	-0.0731 (2)	0.2576 (7)	0.1334 (2)	3.18*
C23	-0.0985 (2)	0.2832 (8)	0.1876 (2)	3.52*
C24	-0.0900 (2)	0.1078 (8)	0.2288 (2)	3.54*
C25	-0.0558 (2)	-0.0923 (8)	0.2164 (2)	3.50*
C26	-0.0301 (2)	-0.1163 (7)	0.1624 (1)	2.83*
O1	-0.1080 (1)	-0.3626 (5)	0.0113 (1)	4.21*
O2	-0.1704 (1)	-0.0852 (5)	0.0481 (1)	3.96*
H12	0.090 (2)	0.290 (7)	0.139 (2)	4.9 (10)
H13	0.179 (2)	0.272 (7)	0.213 (2)	5.0 (9)
H14	0.253 (2)	-0.053 (6)	0.219 (1)	4.4 (8)
H15	0.232 (2)	-0.363 (7)	0.146 (2)	5.3 (10)

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Atom	x	y	z	B
H16	0.142 (2)	-0.355 (7)	0.072 (1)	4.8 (8)
H22	-0.080 (2)	0.376 (6)	0.104 (1)	4.1 (8)
H23	-0.121 (2)	0.429 (7)	0.194 (2)	5.2 (10)
H24	-0.106 (2)	0.125 (6)	0.267 (2)	4.7 (9)
H25	-0.050 (2)	-0.225 (8)	0.247 (2)	7.1 (12)
H26	-0.006 (2)	-0.247 (7)	0.152 (1)	4.0 (9)
H51	-0.257 (3)	-0.184 (9)	0.074 (2)	8.0 (13)
H52	-0.194 (2)	-0.282 (10)	0.111 (2)	8.9 (16)
H53	-0.214 (3)	-0.404 (10)	0.043 (2)	10.8 (20)
H3	-0.097 (1)	0.182 (5)	0.012 (1)	1.8 (6)

* These are equivalent isotropic temperature factors corresponding to the anisotropic parameters listed in Table 15.

Table 15

Anisotropic Temperature Factors ($\text{\AA}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0.035(2)	0.025(2)	0.024(2)	0.002(2)	0.004(1)	-0.001(2)
C2	0.037(2)	0.028(2)	0.022(2)	-0.002(2)	0.004(2)	0.001(2)
C3	0.028(2)	0.034(2)	0.025(2)	0.005(2)	0.004(1)	0.001(2)
C4	0.028(2)	0.050(3)	0.026(2)	0.002(2)	0.002(2)	0.004(2)
C5	0.047(3)	0.108(5)	0.070(3)	-0.020(4)	0.024(3)	0.016(4)
C11	0.029(2)	0.034(2)	0.025(2)	-0.004(2)	0.005(1)	0.000(2)
C12	0.036(2)	0.040(3)	0.034(2)	0.005(2)	0.007(2)	-0.002(2)
C13	0.042(2)	0.056(3)	0.038(2)	-0.009(2)	0.003(2)	-0.008(2)
C14	0.038(2)	0.063(3)	0.041(2)	-0.002(3)	-0.004(2)	0.000(2)
C15	0.046(2)	0.046(3)	0.051(2)	0.012(2)	-0.002(2)	0.003(2)
C16	0.049(2)	0.038(3)	0.037(2)	0.012(2)	0.000(2)	-0.003(2)
C21	0.027(2)	0.038(2)	0.024(2)	-0.003(2)	0.004(2)	-0.002(2)
C22	0.049(2)	0.040(3)	0.033(2)	0.004(2)	0.010(2)	0.000(2)

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Table 15 continued

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C23	0.047(2)	0.048(3)	0.040(2)	0.007(2)	0.009(2)	-0.006(2)
C24	0.046(2)	0.059(3)	0.031(2)	-0.009(2)	0.013(2)	-0.007(2)
C25	0.047(2)	0.055(3)	0.032(2)	-0.002(2)	0.011(2)	0.007(2)
C26	0.036(2)	0.040(3)	0.032(2)	0.005(2)	0.007(2)	0.005(2)
O1	0.062(2)	0.036(2)	0.065(2)	-0.004(2)	0.021(1)	-0.003(2)
O2	0.035(1)	0.062(2)	0.057(2)	-0.001(2)	0.019(1)	0.000(2)

Table 16Interatomic Distances ($\text{\AA}$)

C1 - C2	1.326(4)	C4 - O1	1.194(4)
C1 - C3'	1.513(4)	C4 - O2	1.336(4)
C2 - C3	1.523(4)	C5 - O2	1.462(5)
C1 - C11	1.501(4)		
C2 - C21	1.502(4)	C12 - H12	0.95(4)
C3 - C4	1.537(5)	C13 - H13	1.01(4)
C3 - H3	0.98(3)	C14 - H14	1.02(3)
		C15 - H15	1.00(4)
C11 - C12	1.395(5)	C16 - H16	1.06(4)
C12 - C13	1.402(5)	C22 - H22	0.95(4)
C13 - C14	1.374(5)	C23 - H23	0.98(4)
C14 - C15	1.386(5)	C24 - H24	0.95(3)
C15 - C16	1.395(5)	C25 - H25	1.03(4)
C16 - C11	1.387(5)	C26 - H26	0.93(4)
C21 - C22	1.387(5)		
C22 - C23	1.390(5)	C5 - H51	1.03(5)
C23 - C24	1.378(5)	C5 - H52	0.92(5)
C24 - C25	1.384(5)	C5 - H53	1.04(5)
C25 - C26	1.387(5)		
C26 - C21	1.390(5)		

Table 17
Intramolecular Angles

<u>Atoms</u>	<u>Angle</u>	<u>Atoms</u>	<u>Angle</u>
C3' - C1 - C2	122.4(3)	C22 - C21 - C26	118.6(3)
C3' - C1 - C11	113.7(3)	C21 - C22 - C23	120.9(4)
C11 - C1 - C2	124.4(3)	C22 - C23 - C24	119.8(4)
C1 - C2 - C3	122.1(3)	C23 - C24 - C25	120.0(4)
C1 - C2 - C21	124.4(3)	C24 - C25 - C26	120.0(4)
C21 - C2 - C3	113.4(3)	C25 - C26 - C21	120.7(4)
C2 - C3 - C1'	115.4(3)		
C2 - C3 - C4	106.1(3)	C3 - C4 - O1	124.7(4)
C2 - C3 - H3	110(2)	C3 - C4 - O2	110.6(3)
C1' - C3 - C4	108.4(3)	O1 - C4 - O2	124.7(4)
C1' - C3 - H3	110(2)	C4 - O2 - C5	115.4(4)
C4 - C3 - H3	107(2)		
		H12 - C12 - C11	122(2)
C1 - C11 - C12	120.6(3)	H12 - C12 - C13	118(2)
C1 - C11 - C16	120.3(3)	H13 - C13 - C12	119(2)
C12 - C11 - C16	119.0(3)	H13 - C13 - C14	120(2)
C11 - C12 - C13	120.1(4)	H14 - C14 - C13	119(2)
C12 - C13 - C14	120.4(4)	H14 - C14 - C15	121(2)
C13 - C14 - C15	119.6(4)	H15 - C15 - C14	123(2)
C14 - C15 - C16	120.5(4)	H15 - C15 - C16	117(2)
C15 - C16 - C11	120.3(4)	H16 - C16 - C15	118(2)
C2 - C21 - C22	119.8(3)	H16 - C16 - C11	122(2)
C2 - C21 - C26	121.4(3)	H22 - C22 - C21	119(2)

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Table 17 continued

<u>Atoms</u>	<u>Angle</u>	<u>Atoms</u>	<u>Angle</u>
H22 - C22 - C23	120(2)	H26 - C26 - C21	117(2)
H23 - C23 - C22	117(2)	O2 - C5 - H51	103(3)
H23 - C23 - C24	123(2)	O2 - C5 - H52	105(3)
H24 - C24 - C23	121(2)	O2 - C5 - H53	107(3)
H24 - C24 - C25	119(2)	H51 - C5 - H52	106(4)
H25 - C25 - C24	120(2)	H52 - C5 - H53	121(5)
H25 - C25 - C26	120(2)	H53 - C5 - H51	112(4)
H26 - C26 - C25	123(2)		

Table 18Intramolecular Non Bonded Contacts

<u>Atoms</u>	<u>Distance</u>
C1' - C4	2.474 (5)
C2 - C4	2.445 (5)
C1 - C1'	2.888 (6)
C2 - C2'	2.888 (6)
C3 - C3'	2.947 (7)
C1 - C3	2.496 (5)
C2 - C3'	2.489 (5)
C1 - C2'	2.566 (4)
C11 - C21	3.013 (5)
C11 - C26	3.251 (5)
C21 - C12	3.148 (5)
C12 - C26	3.416 (5)
C11 - O1'	3.360 (4)
C21 - O2	3.090 (4)
C22 - O2	3.273 (5)
O1 - O2	2.242 (4)
C4 - C11	2.993 (5)
C4 - C21	2.916 (5)
H12 - O1'	3.49 (4)
H22 - O2	3.39 (3)
H3 - H16'	2.27 (4)
H3 - H22	2.37 (4)

Table 19
Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation	Distance
C22	C26	$x, 1+y, z$	3.750 (5)
C23	C25	$x, 1+y, z$	3.740 (5)
C23	C26	$x, 1+y, z$	3.785 (5)
C12	C16	$x, 1+y, z$	3.811 (5)
C13	C15	$x, 1+y, z$	3.823 (5)
O1	C3	$x, 1-y, z$	3.534 (5)
C5	H15	$x-1/2, -y-1, z$	3.01 (4)
C5	H53	$-1/2-x, y, -z$	3.01 (5)
C13	H51	$1/2+x, -y, z$	3.04 (5)
C14	H51	$1/2+x, -y, z$	3.01 (5)
C15	H51	$1/2+x, -y, z$	3.03 (5)
C15	H24	$-x, y-1/2, 1/2-z$	3.03 (4)
C24	H25	$-x, 1/2+y, 1/2-z$	2.96 (4)
O1'	H16	$x, y-1, z$	2.54 (4)
O1	H22	$x, y-1, z$	2.61 (4)
O1	H3	$x, y-1, z$	2.63 (3)
H13	H14	$1/2-x, 1/2-y, 1/2-z$	2.54 (5)
H13	H24	$-x, 1/2+y, 1/2-z$	2.57 (5)
H24	H13	$-x, y-1/2, 1/2-z$	2.57 (5)
H53	H53	$-1/2-x, y, -z$	2.3 (1)

Table 20
Least Squares Planes

(1) Atoms defining plane. C1 C2 C3 C1' C2' C3'

Equation of plane. $0.1449X + 0.9867Y - 0.0741Z = 0$

Distances of atoms from plane in Å

C1	-0.012(3)
C2	0.011(4)
C3	-0.012(4)
C1'	0.012(3)
C2'	-0.011(4)
C3'	0.012(4)

$\chi^2 = 62.46$ - Hypothesis that these atoms lie in the least squares plane can be rejected at the 99.9% confidence level.

(2) Atoms defining plane. C1 C2 C1' C2'

Equation of plane. $0.1617X + 0.9838Y - 0.0768Z = 0$

Distances of atoms from plane in Å

C1, C2, C1', C2'	0.0
------------------	-----

Distances of other atoms from plane in Å

C3	-0.037(4)
C3'	0.037(4)
C11	-0.001(4)
C21	-0.044(4)

(Continued on next page)

Table 20 continued

(3) Atoms defining plane. C3 C4 O1 O2 C5

$$\text{Equation of plane. } -0.4428X + 0.1145Y - 0.8893Z - 0.4970 = 0$$

Distances of atoms from plane in Å

C3	-0.044(3)
C4	0.023(3)
O1	0.007(3)
O2	0.039(2)
C5	-0.186(6)

(4) Atoms defining plane. C11 C12 C13 C14 C15 C16

$$\text{Equation of plane. } 0.6475X + 0.4693Y - 0.6005Z + 0.1848 = 0$$

Distance of atoms from plane in Å

C11	-0.002(3)
C12	0.003(4)
C13	-0.004(4)
C14	0.003(4)
C15	-0.001(4)
C16	0.001(4)

(Continued on next page)

Table 20 continued

Distances of other atoms from plane in Å^o

H12	0.05(4)
H13	0.02(4)
H14	0.03(3)
H15	0.02(4)
H16	-0.02(3)

(5) Atoms defining plane. C21 C22 C23 C24 C25 C26

Equation of plane. $-0.8239X - 0.4139Y - 0.3812Z + 0.3213 = 0$

Distances of atoms from planes in Å^o

C21	-0.003(3)
C22	0.005(4)
C23	-0.004(4)
C24	0.000(4)
C25	0.002(4)
C26	0.001(4)

Distances of other atoms from plane in Å^o

H22	0.04(3)
H23	-0.03(4)
H24	-0.03(3)
H25	0.02(4)
H26	-0.01(3)

(Continued on next page)

Table 20 continued

(6) Atoms defining plane. C3, C2, C21, C1, C11, C3'

Equation of plane. $0.1462X + 0.9871Y - 0.0651Z - 0.0041$
 $= 0$

Distances of atoms from plane in Å

C3	-0.016(4)
C2	0.019(4)
C21	0.001(4)
C1	-0.004(3)
C11	-0.010(4)
C3'	0.007(4)

Table 21

A Survey of Literature Values for
C = C and C_(sp³) - C_(sp²) Bond Lengths

Compound	C = C	C _(sp³) - C _(sp²)	Reference
4-Diethyl carbamoyl- -1-cyclohexene-5- carboxylic acid	1.322	1.503	73
Cyclohexene	1.335	1.504	74
Bicyclohexylidene	1.332	1.518	75
Cyclooctatetraene carboxylic acid	1.322	-	76
Octaphenyl cyclo- octatetraene	1.343	-	77
cis,cis,cis-1,4,7- cyclononatriene	1.34	1.52	78
Hydrobromide of 1-p- (2-Dimethylamino- ethoxy-phenyl)-1,2-cis- diphenylbut-1-ene	1.33	1.52	79
8,12-Diethyl-2,3,7,13, 17,18-hexamethylcorrole	-	1.507	80
Tazettine Methiodide	1.33	1.52	81
1,1-Di-(p-nitrophenyl) ethylene	1.326	-	82
Cyclohexa-1,4-diene	1.330	1.498	65
Cyclohexa-1,4-diene	1.347	1.511	66
1,3-Cyclohexadiene	-	1.523	66
1,4-Cyclohexadiene-1- glycine	1.347	1.485	69
Weighted Average	1.333	1.509	

Table 22

A Selection of Carboxylic Acid and Ester Group Geometries

Compound Name	C=O	C-O	O-C _{est}	C _α -C=O	C _α -C-O	C _{est} -O-C	O=C-O	Reference
1,1,2,2-tetracarbo-methoxyethane	1.192 1.188	1.324 1.317	1.453 1.461	125.0 123.6	109.6 110.9	114.6 116.4	125.4 125.5	88
Salicylic Acid	1.234	1.307	-	122.9	116.0	-	121.2	89
Acetyl Salicyclic Acid	1.183	1.364	1.402	126.4	110.7	115.7	122.9	90
Trans-1,3-cyclobutane dicarboxylic acid	1.238	1.345	-	124.1	113.0	-	122.9	91
(±)-trans-1,2-cyclohexane dicarboxylic acid	1.209	1.314	-	123.5	113.1	-	123.3	92
trans-bicyclo[4.2.0]octyl-1-3,5-dinitrobenzoate	1.200	1.323	1.486	122.0	111.1	117.2	126.9	93
3'-O-acetyladenosine	1.200	1.358	1.445	125.7	110.6	116.6	123.7	94

(Continued on next page)

Table 22 continued

Compound Name	C=O	C-O	O-C _{est}	$\hat{C}\alpha-\hat{C}=O$	$\hat{C}\alpha-\hat{C}-O$	C _{est} -O-C	O=C-O	Reference
1,2,4,5-tetraphenyl- 3,6-dicarbomethoxy- tricyclo[3.1.0.0 ^{2,4}] hexane	1.200	1.329	1.449	126.2	110.0	116.2	123.8	This work (Chapter 3)
1,2,4,5-tetraphenyl- 3,6-dicarbomethoxy- cyclohexa-1,4-diene	1.194	1.336	1.462	124.7	110.6	115.4	124.7	This work

Fig. 4

A Perspective View of the 1,2,4,5-tetraphenyl-
3,6-dicarbomethoxycyclohexa-1,4-diene molecule

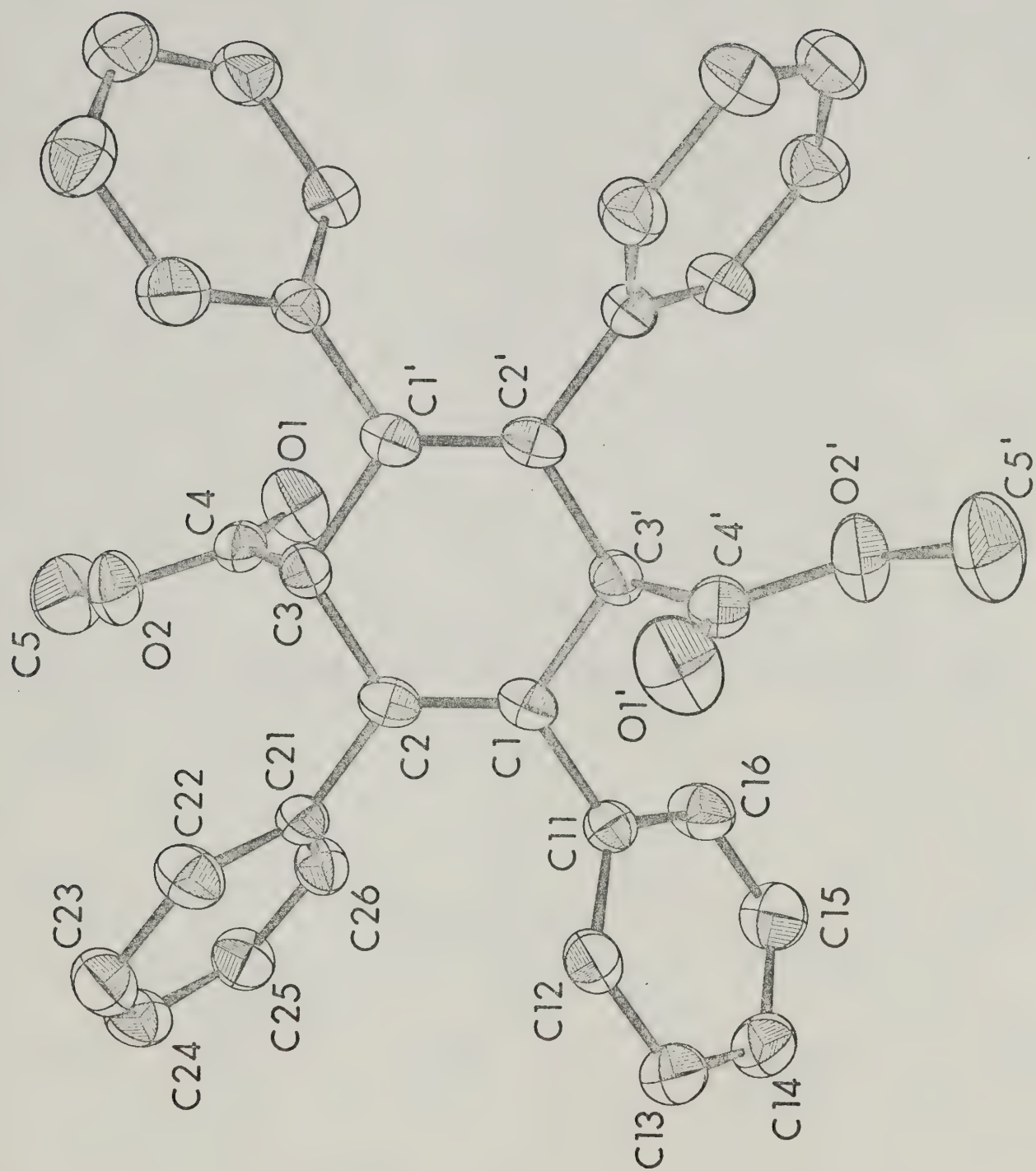


Fig. 5

Contents of the Unit Cell Projected onto the $[a][b]$ Plane

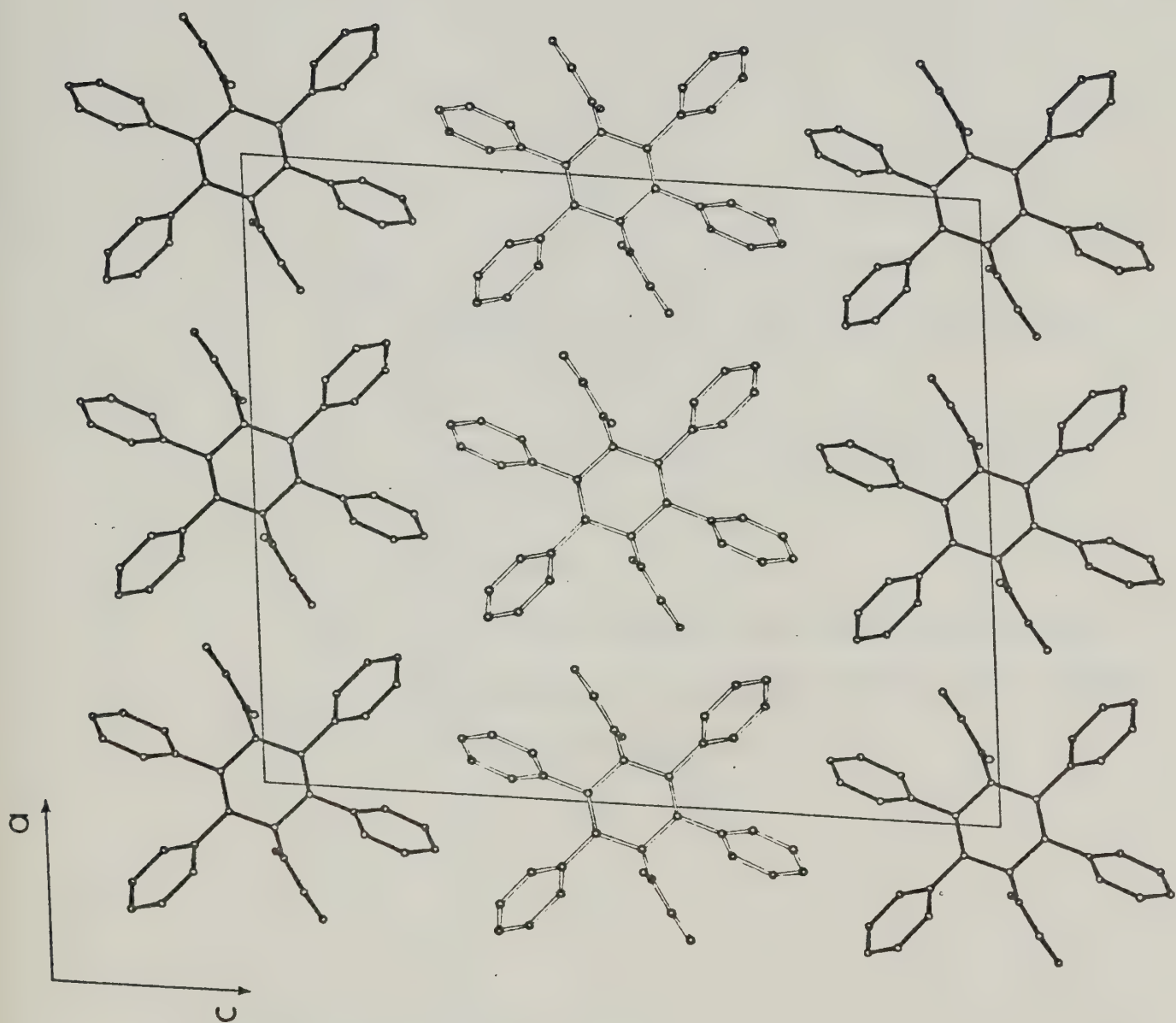
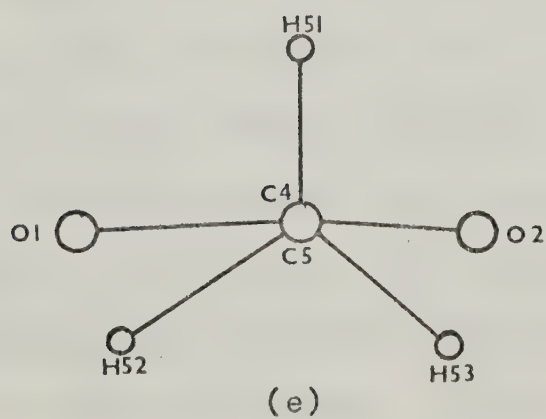
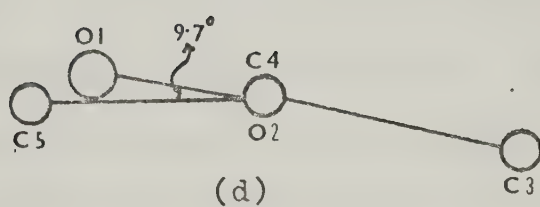
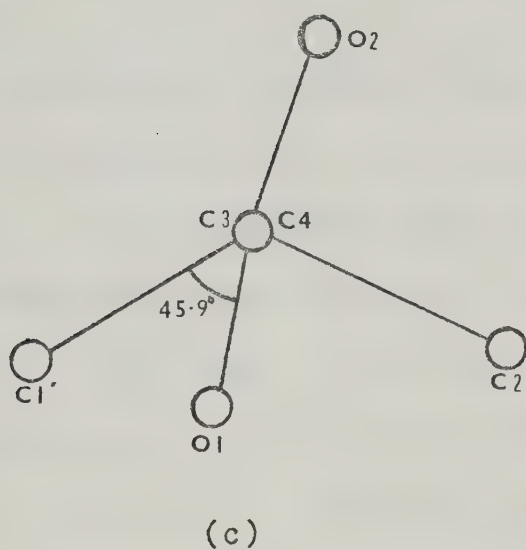
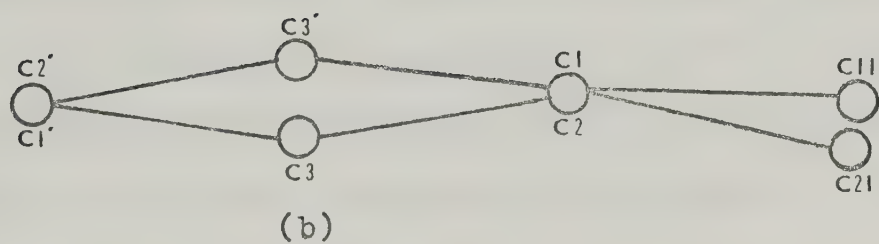
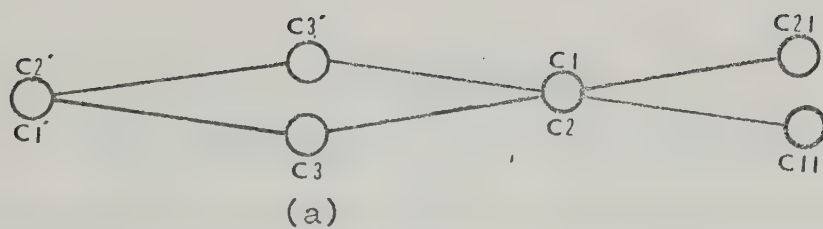


Fig. 6

A Selection of Newman Projections:

- (a) theoretical view down C2-C1 for slight chair conformation
- (b) actual view down C2-C1 (exaggerated)
- (c) down C3-C4
- (d) down O2-C4
- (e) down C5-C4 virtual bond showing partial staggering of hydrogen atoms with respect to carbonyl oxygen



DISCUSSION

The molecule is shown in Fig. 4. It crystallises with the cyclohexadiene ring occupying a crystallographic inversion centre, with the plane of the ring almost perpendicular to the b axis. Because it occupies an inversion centre, the compound is necessarily *anti*-1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene and any deviations from planarity of the cyclohexadiene ring lead to a chair not a boat form.

The double bonds in the cyclohexadiene ring have a length of 1.326 Å, while the single bonds average 1.518 Å. This is not in particularly good agreement with the geometry found by Jandacek and Simonsen, who obtained average bond lengths of 1.347 Å and 1.485 Å for the double and single bonds respectively in the cyclohexadiene ring of 1,4-cyclohexadiene-1-glycine⁶⁹. However, the large standard deviations on the bond lengths in their structure render the differences insignificant. The results are, however, in good agreement with values commonly found in the literature. A survey of twelve structures containing unconjugated carbon-carbon double bonds and ten containing C(sp³) - C(sp²) single bonds, gave a range of values from 1.312 Å to 1.347 Å with an average of 1.333 Å for the double bond, and 1.485 Å to 1.523 Å with an average of 1.509 Å for the single bond (Table 21). The double and single bond lengths in the cyclohexadiene ring can therefore be taken as normal. The bond angles within the cyclohexadiene ring are essentially the same as those found by

Jandaceck and Simonsen.

The exocyclic bonds to the phenyl rings have lengths 1.501 and 1.502 Å which is similar to that found in two independent structure determinations of octaphenyl cyclooctatetraene^{77,83} and in hexaphenyl benzene⁸⁴, where the exocyclic bond lengths to phenyl rings average 1.50 Å. The angles that these bonds make with the double bond of the cyclohexadiene ring of 124.4° are slightly larger than those normally found around sp² hybridised carbon atoms. The widening of this bond angle serves to decrease the intramolecular repulsion between the phenyl rings. A similar situation is again observed in octaphenyl cyclooctatetraene.

Both the phenyl rings are planar within experimental error and the hydrogen atoms associated with them all lie in these planes. The average C - C bond length in these rings is 1.388 Å and the C - H bond length is 0.99 Å. The average C - C - C angle is 120.0° and the average H - C - C angle is 120°, all of which are very close to accepted values. The phenyl rings are rotated by angles of 52.2° and 58.7° respectively from a position which would be coplanar with the plane containing the two ethylenic bonds.

The preferred conformation of the ester group with the C = O, synplanar with respect to the C_α - C_β bond, i.e. with the torsion angle C_β - C_α - C = O equal to or close to zero⁸⁵⁻⁸⁷, cannot be attained in this compound because of

steric interference by the phenyl rings. This steric interference causes the carbomethoxy group to rotate about the $C_4 - C_3$ bond, giving a torsion angle of 45.9° for $C_1' - C_3 - C_4 = O_1$, to what is perhaps an optimum position, minimising intramolecular interaction between the two oxygen atoms and the phenyl rings and intermolecular contacts between O_1 and the phenyl ring attached to C_1' one unit cell beneath it. At the same time these forces affect the geometry at C_3 slightly. Angle $C_2 - C_3 - C_4$ is 106.1° , significantly smaller than the 108.4° angle of $C_1' - C_3 - C_4$. This reduces intramolecular contact between O_1 and the phenyl ring attached to C_1' but increases that between O_2 and the phenyl ring attached to C_2 . This may account for the greater rotation of this phenyl group with respect to the plane containing the ethylenic linkages. The bond length $C_3 - C_4$ is $1.537 \text{ \AA}$ which is $0.02 - 0.03 \text{ \AA}$ longer than that commonly observed in the literature for this type of bond. No satisfactory explanation can be provided for this, other than that once again, the lengthening of this bond reduces intramolecular non-bonded interaction between the phenyl rings and the carbomethoxy group. The position thus taken up by the carbomethoxy group is such that the minimum intramolecular contact between O_2 and phenyl ring 2 is $3.090 \text{ \AA}$ between O_2 and C_{21} , and that between O_1 and phenyl 1' is 3.360 between O_1 and C_{11}' . The closest O_1 -phenyl intermolecular contact is $O_1 - H_{16}'$ of $2.54 \text{ \AA}$.

The bond lengths and angles within the ester group

are similar to those found in the literature (Table 22). The group is close to being planar, but the deviations from the best plane through the five atoms C_3 , C_4 , O_1 , O_2 , C_5 , although small, are significant (Table 8), with C_5 lying $0.186 \text{ \AA}$ out of this plane. The carbonyl group does not eclipse the methyl group, the torsional angle $O = C - O - CH_3$ being 9.7° , and the hydrogens of the methyl group are only partially staggered with respect to the $C = O$ bond. Thus the carbomethoxy group does not take up the accepted conformation for primary esters^{87,95}, probably due to the intra- and intermolecular forces acting upon it.

The cyclohexa-1,4-diene ring has small but significant deviations from planarity (Table 20), each of the six atoms lying 0.011 to $0.012 \text{ \AA}$ out of the least squares plane. If we define the reference plane as the one containing the four olefinic (C_{sp^2}) carbon atoms, then the deviation of the methylenic (C_{sp^3}) carbon atom from this plane is $0.037 \text{ \AA}$. The dihedral angle between the plane formed by $C_2 C_3 C_1'$ and that by $C_1 C_2 C_1' C_2'$ is 177.4° . This agrees well with the electron diffraction work of Dallinga and Toneman⁶⁵, who refined a planar form of the molecule to completion but could not rule out the possibility that other nearly planar conformations, especially the chair form, were present, with a maximum deviation from the plane of $0.05 \text{ \AA}$. The results are, however, in disagreement with the electron diffraction study of Oberhammer and Bauer⁶⁶, who concluded that the molecule

had a pronounced boat conformation.

However, one must always be cautious when extrapolating results obtained from solid state studies to molecules in the liquid or gaseous phase. While the cyclohexa-1,4-diene ring in this structure is not severely constrained, as it would be in a fused ring system, the question remains as to whether the slight chair conformation is a preferred conformation, or whether it is imposed upon the ring as a result of either intermolecular forces in the condensed phase or intramolecular forces due to the bulky substituents.

The intermolecular forces would appear not to be responsible. The closest C---C contacts occur between phenyl rings and are all greater than $3.74 \text{ \AA}$. The closest carbon-hydrogen contacts are about $3.0 \text{ \AA}$ or more, and hydrogen-hydrogen contacts are $2.54 \text{ \AA}$ or greater. All these distances are greater than the sum of the Van der Waals radii of the atoms concerned. The intermolecular interaction between the carbonyl oxygen and the methylenic carbon atom and its hydrogen atom in the molecule one unit cell away in the b direction also is not important. The $O_1\text{---}H_3$ distance of $2.63 \text{ \AA}$ and the $O_1\text{---}C_3$ distance of $3.533 \text{ \AA}$ are both greater than the sum of the Van der Waals radii of the atoms involved, $2.6 \text{ \AA}$ and $3.1 \text{ \AA}$ respectively.

Intramolecular forces, on the other hand, are very important in this sterically overcrowded molecule. The phenyl-phenyl repulsions are reduced to some extent by the widening

of the $C_{\text{phen}} - C = C$ angle. Of course, they would be further reduced by the adoption of a slight chair conformation by the molecule, since, normally, this would lead to a slightly staggered conformation of C_{11} and C_{21} with respect to the olefinic bond. It should be noted that this distortion would be expected to lead to a slight reduction in the π -bond overlap. However, an examination of the olefinic plane (Table 20) indicates that this is not the case in this structure. The deviations from the least squares plane are not what would be expected for the normal chair structure. The situation is shown, much exaggerated, in Fig. 6(a) and (b). If we again use the plane defined by the four ethylenic carbon atoms as the reference plane, then C_3 and C_3' lie $0.037 \text{ \AA}$ below and above this plane respectively. For the chair structure, one would expect deviations opposite in sign for C_{21} and C_{11} and of more or less the same magnitude as for C_3 and C_3' . Also, C_{21} should lie on the opposite side of the plane to C_3 , and C_{11} should lie on the opposite side of the plane to C_3' (Fig. 6a). However, the deviations of these atoms from the plane (Table 20) are $0.0015 \text{ \AA}$ for C_{11} which is smaller than expected, but in the right direction and $0.044 \text{ \AA}$ for C_{21} which is slightly larger than expected, and in the wrong direction (Fig. 6b). The atoms C_{11} and C_{21} , therefore, have assumed positions closer to what one would expect for a completely planar or even boat form of the molecule. This situation lends itself to two possible interpretations:

(a) The inter- and intramolecular forces are attempting to constrain the molecule in a planar or boat conformation and despite this, the ring retains a slight chair conformation; or,

(b) The preferred conformation is that assumed by the substituents and the inter- and intramolecular repulsive interactions are forcing the ring to take up a chair conformation.

Examination of the intramolecular contacts between the phenyl rings and the carbomethoxy group greatly favour the latter interpretation. The $C_4 \cdots C_{21}$ and $C_4 \cdots C_{11}'$ distances are 2.916 and 2.993 Å respectively, significantly shorter than the Van der Waals contact of 3.4 Å and are, therefore, repulsive in nature. Since C_4 lies further below the plane of the four ethylenic carbon atoms than do C_{11}' and C_{21} , the effect of this repulsive interaction would be to force it even further below the plane, which in turn will cause C_3 to move below this plane. The centrosymmetrically related C_3' will be correspondingly raised above the plane, thus leading to a chair conformation.

Because of the possibility that the conformation of the cyclohexa-1,4-diene ring may be forced upon it by intramolecular forces between the bulky substituents, this molecule is particularly unsuitable for conformational studies concerning the planarity of the cyclohexa-1,4-diene ring.

The packing of the molecule in the [a.c.] plane is shown in Fig. 5. The phenyl rings of molecules related by a

two-fold axis are in the 'herring bone' arrangement commonly found for aromatic groups. There are very few close contacts between molecules in either the a or c direction, the closest packing being in the b direction where the cyclohexadiene rings are parallel to each other and with the normal to the plane of the ring almost coincident with the b axis. There are no intermolecular contacts between molecules smaller than one would expect assuming all intermolecular forces are of the Van der Waals type. The closer intermolecular contacts are shown in Table 7 together with the symmetry relationship between the two molecules involved.

Chapter Three

The Crystal and Molecular Structures of
1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-
tricyclo[3.1.0.0^{2,4}]hexane

INTRODUCTION

The 1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-[3.1.0.0^{2,4}] tricyclohexane was prepared as described on page 76 by Dr. S. Masamune and co-workers. Similar compounds have been prepared by other workers⁹⁶⁻¹⁰². The stereochemistry of the products, however, was either undetermined or assigned only on the basis of mechanistic considerations or n.m.r. studies which left the assigned stereochemistry, at least, uncertain. The X-ray crystal structure of the [3.1.0.0^{2,4}]-tricyclohexane derivative was undertaken in order to unambiguously determine its stereochemistry and also to determine the precise geometry of the novel strained tricyclo system, since it affords the opportunity of observing the effect of ring fusion upon the geometry of the cyclopropane and cyclobutane rings. In cyclobutane it has been observed that the geometry is in general dependent upon the environment in which it is found, the effect of fusion with other rings varying, depending upon the nature of the fusing rings¹⁰³. The effect of ring fusion upon the geometry of the cyclopropane ring does not appear to have received much attention up to this time.

EXPERIMENTAL

The crystals, which approximated hexagonal needles, were supplied by Dr. S. Masamune. One, which was regarded as suitable for photographic work and data collection, was mounted on glass fibre (maximum dimensions 0.17 mm x 0.12 mm x 0.07 mm). Weissenberg photographs were obtained for the $Ok\ell$, $l k\ell$ and $2k\ell$ layers and precession photographs for the $hk0$, $hk\ell$, and hll layers. These showed the Laue symmetry to be $2/m$ and the crystals to be monoclinic. The following systematic absences:

- (1) $h0\ell$ $h + \ell = 2n + 1$ implying an n glide perpendicular to b
 - (2) $0k0$ $k = 2n + 1$ implying a 2_1 axis parallel to b
- defined the space group uniquely as $P_{2_1/n}$ (non standard setting of $P_{2_1/c}$).

The lattice parameters were obtained by the least squares refinement of the 2θ values for several high angle reflections. The 2θ values were measured on a PICKER manual four circle diffractometer. The dimensions obtained were: $a = 10.044(4)$; $b = 9.500(2)$; $c = 14.172(4)$; $\beta = 104.38(2)$.

The experimentally observed density of 1.28 obtained by flotation in aqueous potassium iodide solution agrees well with the calculated density of 1.27 assuming two molecules of molecular weight 500 in a cell of volume $1309.90 \text{ \AA}^3$. The density therefore required that the molecule occupied a crystallographic inversion centre, which eliminated 9 (Chapter 3 p 78) as a possible structure.

Intensity data were collected on a PAILRED automatic

diffractometer using crystal monochromated CuK_α radiation and included the layers $nk\ell$ for $n = 0$ to 8. A constant scan rate of $2.5^\circ/\text{min}$ was used throughout the data collection, but the scan width varied from 1.4° at $h = 0$ to 2.7° at $h = 8$. A stationary background count was taken for 20 secs on each side of the scan.

In the data reduction process, reflections were rejected if, (i) $I = 0$ (ii) $I \leq 3\sigma$. Of the 1316 reflections measured, 478 were rejected in this way giving 838 observed reflections. Measurement of five standard reflections at the end of each layer indicated no significant decomposition took place during the data collection.

An absorption correction was not applied, the linear absorption coefficient for this compound was quite small, being only 6.67 cm^{-1} .

Lorentz and polarisation corrections were applied and structure factor amplitudes and standard deviations were calculated.

During the course of the subsequent structure determination and refinement, it became clear that the data for several layers were very poor. Consequently the data were re-collected using a PICKER manual four circle diffractometer.

Crystal monochromatised CuK_α radiation was used and the intensity data collected using the coupled $\omega/2\theta$ scanning technique. The scan width was 3° with a scan rate of $2^\circ/\text{min}$ and a 2θ maximum of 120° . A stationary background count was

taken for 20 secs on each side of the scan.

Reflections were again rejected if $I \leq 0$ or if $I \leq 3\sigma$. 932 of the 1958 reflections collected were rejected in this manner giving 1032 observed reflections.

Lorentz and polarisation corrections were applied, but no correction for absorption was made. Structure factor amplitudes and standard deviations were then calculated.

SOLUTION OF STRUCTURE AND REFINEMENT

The structure was solved, using the PAILRED data, by direct methods. The symbolic addition was performed using the N.R.C. system of programmes SAP1 - 4(b).

Normalised structure factors were calculated (page 20) and their distribution shown below, was clearly in agreement with the known centrosymmetric space group.

	This Structure	Centrosymmetric	Non Centrosymmetric
$\langle E \rangle$	0.825	0.798	0.886
$\langle E ^2 \rangle$	0.969	1.000	1.000
$\langle E ^2 - 1 \rangle$	1.058	0.968	0.736
Percentage $ E > 3$	0.84	0.30	0.01
Percentage $ E > 2$	5.55	5.00	1.80
Percentage $ E > 1$	28.57	32.00	37.00

Three reflections were arbitrarily given positive signs and used to define the origin, and to initiate the symbolic addition procedure. These were:

<u>Reflection</u>	<u>E</u>
1 3 -1	3.238
2 1 1	3.816
1 0 -3	2.919

The acceptance level for a sign determination was set initially at $\sum_k \sigma_3 \sigma_2^{-3/2} |E_h| E_k E_{h-k} = 7.9$ and was allowed

to fall slowly during the sign determination to a minimum acceptable value of 1.9 which corresponds to a probability of 0.978.

When the acceptance level had fallen to 6.4 and no new signs had been determined, symbol A was assigned to reflection $2\ 5\ -3$ ($|E| = 3.587$). At 4.9 B was assigned to $1\ 8\ 2$ ($|E| = 3.263$) and at 3.4 C was assigned to $2\ 1\ 0$ ($|E| = 3.851$).

118 reflections were assigned phases in terms of these three symbols. During the phase determining procedure, several relationships between symbols occurred. Such relationships were accepted if both contributors had $\sum_k \sigma_3 \sigma_2^{-3/2} |E_h| E_k E_{h-k}$ greater than 1.9. These relationships are summarised in the table below.

Symbol	No. of Indications +ve	No. of Indications -ve
A	1	2
B	0	7
AB	0	0
C	0	3
AC	0	1
BC	4	2
ABC	5	0

From these relationships, it was possible to say confidently that $B = -$ and $ABC = +$, which meant that A and C were opposite in sign. The indication seemed to be that C

was negative and therefore A positive, but E_{maps} corresponding to both possible solutions, (i) $A = +$, $B = -$, $C = -$ and (ii) $A = -$, $B = +$, $C = +$, were computed. In the first of these maps, the structure was eventually recognised, but not without difficulty due to the presence of several quite large but meaningless peaks. All the atoms were located in this E map apart from four carbon atoms from one of the phenyl rings.

These fifteen atom positions were used as input to a structure factor calculation, which gave a residual R factor of 0.511. The calculated phases were used to compute an electron density map which revealed the positions of the remaining four carbon atoms. At this early stage of the structure determination, the two phenyl rings in the asymmetric unit were refined as rigid bodies with a C - C distance of 1.397 Å and a C - C - C angle of 120°.

In three cycles of refinement the R factor dropped to 0.259, but analysis of the R factor for each level collected showed that the data was suspect. The R factors are shown in tabulated form below:

Level		R_1	R_2
hkl	(all data)	0.259	0.489
hk0		0.199	0.923
h0l		0.246	0.872
0kl		0.218	0.359

(Continued on next page)

Level	R_1	R_2
1kℓ	0.227	0.321
2kℓ	0.238	0.327
3kℓ	0.253	0.314
4kℓ	0.437	1.273
5kℓ	0.296	0.342
6kℓ	0.284	0.393
7kℓ	0.259	0.289
8kℓ	0.264	0.312

Clearly the data for the 4kℓ level contained some very large errors. This data was omitted from the subsequent refinement cycles, and the complete data set was recollected using a PICKER four circle manual diffractometer (see page 122). While the data recollection was in process, the refinement was continued with the PAILRED data minus the 4kℓ reflections.

In two more cycles, the $\bar{R}$ factor reduced to 0.153, at which point, the atoms of the phenyl rings were allowed to refine as free atoms. The R factor fell in one cycle to 0.136. There were indications here that even more of the upper level data was suspect, since the R factors for 5kℓ and 6kℓ were 0.213 and 0.205 respectively.

An electron density difference map was now calculated, and from it, all the hydrogen atom positions in the molecule were obtained without difficulty. Inclusion of these atoms in

the least squares refinement caused the R factor to drop in two more cycles to 0.111.

Two further refinement cycles in which all atoms other than the hydrogen atoms were allowed to refine anisotropically, further reduced the R factor to 0.073.

The data collected on the PICKER diffractometer was now substituted for the faulty PAILRED data. In four cycles the refinement converged with $R_1 = 0.040$, $R_2 = 0.048$.

Inspection of the observed and calculated structure amplitudes of low $\sin \theta/\lambda$ and large magnitude revealed that the crystal was suffering secondary extinction. Since absorption was negligible in this crystal, a correction was made for the polarisation part of the secondary extinction correction only. (See page 89).

After this correction had been applied, the refinement reconverged in two cycles to a final R_1 of 0.038 and $R_2 = 0.038$. The largest peak in an electron density difference map computed at the end of the refinement was only 0.13 electrons per $\text{\AA}^3$ and was situated close to the methyl hydrogens.

Of the 118 signs determined in the symbolic addition procedure, 14 were incorrectly determined, which may account for some of the meaningless peaks in the E map.

RESULTS

The observed and calculated structure amplitudes are listed in Table 23. Atomic coordinates and isotropic temperature factors are given in Table 24 and anisotropic temperature factors for the carbon and oxygen atoms are in Table 25. Bond lengths and angles are given in Tables 26 and 27. A selection of intramolecular and intermolecular non bonded contacts is given in Tables 28 and 29. The geometries of the cyclopropane and cyclobutane rings in various systems are summarised in Tables 30 and 31.

A perspective view of the molecule is given in Fig. 7. The contents of the unit cell projected onto the $[a][c]$ plane is shown in Fig. 8. A selection of Newman projections is shown in Fig. 9.

Table 23

Observed and Calculated Structure Amplitudes (electrons $\times 10$)

K	L	FOHS	FCAL	K	L	FOHS	FCAL	K	L	FOHS	FCAL	K	L	FOHS	FCAL	K	L	FOHS	FCAL
-8	-2	71	67	8	1	66	63	5	1	83	88	5	1	108	101	-2	-8	209	212
-8	-1	57	44	8	5	94	92	5	2	71	73	5	2	115	112	-2	-6	198	144
-7	-10	51	59	9	3	63	65	5	4	98	97	6	0	77	78	-2	-4	166	165
-7	-8	77	77	**H = 5****				5	5	59	40	6	2	159	164	-2	-3	66	51
-7	-7	72	73	-9	-5	66	58	5	6	59	57	6	4	76	75	-1	-13	52	49
-7	-3	129	130	-9	-1	67	72	6	1	116	115	7	0	69	61	-1	-11	105	105
-7	-2	181	181	-8	-8	72	71	6	2	65	61	7	1	97	98	-1	-10	128	135
-6	-9	110	105	-8	-4	86	86	6	3	83	82	8	1	55	52	-1	-7	61	63
-6	-8	111	121	-7	-8	121	123	6	5	74	76	**H = 7****				-1	-6	78	92
-6	-7	87	58	-7	-5	83	78	6	7	57	64	-8	-3	56	55	-1	-5	256	248
-6	-5	66	72	-7	-3	87	86	7	0	172	172	-8	-1	49	56	-1	-4	119	114
-6	-3	80	75	-6	-11	83	78	7	1	55	56	-7	-3	78	85	-1	-3	157	160
-6	-2	138	131	-6	-10	52	55	7	7	48	55	-7	-2	73	65	-1	-2	137	132
-6	-1	150	149	-6	-9	67	79	8	0	126	130	-7	-1	125	125	0	-12	65	69
-5	-13	59	48	-6	-7	196	207	8	1	65	72	-6	-9	78	92	0	-10	83	69
-5	-9	291	295	-6	-6	141	145	8	3	60	55	-6	-8	61	69	0	-8	214	212
-5	-7	57	62	-6	-5	141	140	9	0	60	55	-6	-5	132	140	0	-6	125	116
-5	-6	70	72	-6	-4	140	144	**H = 6****				-6	-4	98	96	0	-4	206	216
-5	-4	151	145	-6	-3	185	182	-8	-4	54	60	-6	-3	137	147	0	0	65	52
-5	-1	123	121	-6	-1	150	146	-7	-10	90	91	-5	-12	63	61	0	2	99	108
-4	-13	88	90	-5	-12	151	140	-7	-7	109	109	-5	-10	93	89	0	4	88	95
-4	-11	84	91	-5	-9	84	76	-7	-6	120	122	-5	-9	68	74	1	0	172	167
-4	-10	76	80	-5	-8	143	139	-7	-4	60	56	-5	-8	81	82	1	1	68	64
-4	-9	102	104	-5	-7	87	96	-7	-3	121	128	-5	-7	100	107	1	2	94	96
-4	-8	71	66	-5	-4	149	141	-7	-1	92	94	-5	-6	80	71	1	3	128	130
-4	-5	149	143	-5	-3	73	79	-6	-11	84	75	-5	-5	153	150	1	4	77	71
-4	-3	48	35	-5	-1	113	113	-6	-9	89	80	-5	-4	158	170	2	0	92	89
-4	-2	241	232	-4	-12	80	79	-6	-7	72	86	-5	-3	81	83	2	4	133	140
-4	-1	66	64	-4	-11	92	96	-6	-6	69	72	-4	-11	132	135	3	2	105	105
-3	-10	320	320	-4	-10	168	171	-6	-5	105	109	-4	-10	70	75	3	3	119	119
-3	-8	83	82	-4	-8	95	100	-6	-3	70	72	-4	-9	70	69	3	4	58	62
-3	-5	169	164	-4	-4	69	59	-5	-12	67	67	-4	-8	60	66	4	1	86	88
-3	-3	70	61	-4	-3	122	113	-5	-8	151	151	-4	-7	130	128	5	0	112	111
-3	-2	345	331	-4	-2	77	77	-5	-7	95	97	-4	-3	117	120	5	1	81	75
-3	-1	122	115	-3	-13	58	69	-5	-5	93	91	-3	-13	97	80	6	2	81	83
-2	-12	205	220	-3	-12	136	139	-5	-4	70	77	-3	-11	82	85	6	3	48	52
-2	-11	63	68	-3	-10	162	164	-5	-3	111	114	-3	-9	59	62	7	1	46	46
-2	-10	110	110	-3	-7	84	84	-5	-2	273	272	-3	-6	73	61	**H = 9****			
-2	-9	159	161	-3	-6	149	155	-5	-1	120	109	-3	-4	133	136	-6	-6	55	35
-2	-8	93	91	-3	-5	308	295	-4	-13	65	63	-3	-3	232	237	-5	-7	71	56
-2	-7	83	89	-3	-4	290	290	-4	-12	52	33	-2	-13	97	101	-5	-6	55	52
-2	-6	220	218	-3	-1	100	105	-4	-10	64	54	-2	-11	75	86	-5	-5	52	57
-2	-5	155	153	-2	-15	50	57	-4	-9	125	125	-2	-10	62	58	-4	-9	83	78
-2	-4	240	231	-2	-13	92	94	-4	-8	100	98	-2	-9	248	241	-4	-7	96	99
-2	-2	66	72	-2	-12	105	110	-4	-5	70	64	-2	-6	156	155	-4	-4	67	66
-2	-1	265	267	-2	-11	132	137	-3	-13	72	71	-2	-5	253	252	-4	-3	114	111
-1	-14	52	76	-2	-10	71	66	-3	-12	154	151	-2	-4	116	118	-3	-11	52	64
-1	-13	114	124	-2	-9	80	78	-3	-9	133	125	-2	-3	330	332	-3	-9	103	107
-1	-11	201	204	-2	-8	98	95	-3	-8	229	233	-2	-1	60	49	-3	-8	75	63
-1	-8	82	82	-2	-7	77	79	-3	-7	71	59	-1	-10	128	131	-3	-7	77	86
-1	-7	53	52	-2	-6	217	213	-3	-6	165	172	-1	-5	75	80	-3	-5	104	95
-1	-6	217	220	-2	-2	166	163	-3	-4	55	69	-1	-3	151	150	-2	-10	101	103
-1	-5	69	67	-2	-1	182	181	-3	-2	67	66	-1	-2	210	207	-2	-6	83	88
-1	-4	121	113	-1	-14	92	92	-2	-9	88	100	0	-13	122	117	-2	-5	90	91
-1	-3	96	99	-1	-13	82	85	-2	-7	110	103	0	-11	122	122	-2	-4	179	181
-1	-2	247	245	-1	-12	75	80	-2	-6	69	70	0	-9	72	82	-2	-3	213	218
-1	-1	62	67	-1	-11	66	72	-2	-5	216	211	0	1	60	74	-2	-2	119	120
0	-12	275	282	-1	-10	68	69	-2	-4	67	51	0	3	107	106	-2	-1	160	164
0	-10	145	144	-1	-7	164	160	-2	-3	120	119	0	7	71	75	-1	-8	150	147
0	-8	116	120	-1	-6	273	266	-2	-1	289	283	1	4	65	71	-1	-6	157	172
0	-4	226	226	-1	-5	289	287	-1	-15	53	44	1	6	56	60	-1	-5	165	166
0	-2	65	33	-1	-4	150	152	-1	-12	56	59	2	1	136	131	0	-11	183	150
0	0	191	166	-1	-2	65	76	-1	-11	94	97	2	3	141	146	0	-7	317	314
0	2	197	204	-1	-1	61	58	-1	-9	113	111	2	4	66	58	0	-5	135	141
0	8	99	58	0	-13	154	161	-1	-8	91	85	2	5	56	46	0	-3	155	153
1	0	422	420	0	-11	84	69	-1	-7	61	62	2	6	69	76	0	-1	103	90
1	1	421	412	0	-9	104	95	-1	-4	131	129	3	0	155	159	1	1	66	68
1	2	380	380	0	-7	370	358	-1	-3	78	60	3	2	61	61	2	1	132	134
1	3	244	250	0	-5	150	147	-1	-2	100	99	3	4	148	153	2	3	107	105
1	5	130	122	0	-3	170	162	-1	-1	80	66	3	5	65	53	2	4	53	60
1	6	91	68	0	-1	270	269	0	-10	82	86	3	6	58	82	3	0	66	70
1	7	176	174	0	1	153	149	0	-8	142	130	4	3	70	69	3	1	54	54
1	8	84	87	0	5	134	125	0	-6	121	123	4	5	89	94	5	0	57	53
1	9	87	92	0	7	110	110	0	-4	82	81	4	7	49	51	**H = 10****			
2	0	277	282	0	9	125	125	0	-2	218	221	5	0	67	67	-4	-7	55	54
2	2	119	128	1	0	350	395	0	0	164	161	5	6	59	65	-4	-5	55	50
2	3	67	77	1	3	89	91	0	2	276	270	5	7	51	49	-4	-4	55	31
2	4	229	223	1	4	111	112	0	6	114	117	6	0	79	78	-3	-9	46	30
2	6	117	127	1	6	155	154	0	10	55	59	6	1	170	168	-3	-2	75	71
2	9	108	58	1	7	129	126	1	0	124	115	6	2	74	69	-2	-10	86	57
3	0	65	50	1	8	157	167	1	2	165	175	6	3	52	31	-2	-6	131	130
3	1	273	269	1	11	46	11	1	3	90	54	6	6	57	62	-2	-5	68	68
3	2	237	237	2	0	248	257	1	7	79	82	**H = 8****				-2	-4	97	55
3	3	47	38	2	1	217	216	1	8	61	69	-7	-1	62	53	-2	-3	56	52
3	4	199	190	2	2	149	151	2	0	132	134	-6	-7	126	119	-1	-8	93	98
3	6	104	114	2	3	181	184	2	1	267	275	-6	-4	62	58	-1	-7	127	120
3	9	122	123	2															

Table 24

Atomic Coordinates and Isotropic Temperature Factors

Atom	x	y	z	B
C1	-0.1037 (3)	-0.0163 (3)	-0.0442 (2)	2.95*
C2	0.0235 (3)	0.0630 (3)	-0.0575 (2)	2.80*
C3	0.0600 (3)	0.1703 (3)	0.0250 (2)	3.11*
C4	0.1672 (3)	0.2756 (4)	0.0210 (2)	3.46*
C5	0.2256 (6)	0.5160 (5)	0.0455 (5)	6.33*
O1	0.2699 (2)	0.2549 (3)	-0.0057 (2)	4.90*
O2	0.1317 (2)	0.4010 (2)	0.0486 (2)	4.51*
C11	-0.2453 (3)	0.0339 (3)	-0.0862 (2)	3.15*
C12	-0.2938 (4)	0.0369 (5)	-0.1865 (3)	4.86*
C13	-0.4242 (4)	0.0872 (5)	-0.2292 (3)	5.51*
C14	-0.5063 (4)	0.1349 (4)	-0.1722 (4)	4.96*
C15	-0.4609 (4)	0.1337 (5)	-0.0744 (4)	5.51*
C16	-0.3300 (4)	0.0844 (4)	-0.0313 (3)	5.09*
C21	0.0556 (3)	0.0841 (4)	-0.1540 (2)	3.04*
C22	0.0286 (4)	0.2130 (4)	-0.2008 (3)	4.26*
C23	0.0496 (4)	0.2329 (5)	-0.2930 (3)	5.03*
C24	0.0977 (4)	0.1249 (4)	-0.3388 (3)	4.64*
C25	0.1237 (4)	-0.0034 (4)	-0.2946 (3)	4.56*
C26	-0.0241 (4)	-0.0241 (4)	-0.2030 (3)	3.91*
H51	0.223 (5)	0.533 (5)	-0.018 (3)	8.2 (16)
H52	0.319 (4)	0.490 (5)	0.080 (3)	7.4 (13)

(Continued on next page)

Table 24 continued

Atom	x	y	z	B
H53	0.190 (5)	0.596 (6)	0.074 (3)	10.5 (17)
HB	-0.012 (3)	0.209 (3)	0.051 (2)	3.6 (7)
H12	-0.238 (4)	-0.001 (4)	-0.228 (2)	6.0 (9)
H13	-0.454 (4)	0.091 (4)	-0.299 (3)	6.4 (10)
H14	-0.596 (4)	0.166 (4)	-0.203 (2)	5.3 (8)
H15	-0.518 (4)	0.156 (4)	-0.030 (3)	6.5 (10)
H16	-0.303 (3)	0.073 (3)	0.032 (2)	4.0 (8)
H22	-0.004 (3)	0.289 (4)	-0.165 (2)	5.4 (8)
H23	0.020 (4)	0.325 (4)	-0.323 (3)	7.2 (10)
H24	0.114 (3)	0.144 (4)	-0.399 (3)	5.7 (10)
H25	0.159 (3)	-0.080 (4)	-0.323 (2)	5.0 (8)
H26	0.119 (3)	-0.110 (3)	-0.176 (2)	3.6 (7)

* These are equivalent isotropic temperature factors corresponding to the anisotropic parameters given in Table 25.

Table 25

Anisotropic Temperature Factors

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0.033(2)	0.038(2)	0.045(2)	0.005(2)	0.018(2)	0.005(2)
C2	0.034(2)	0.033(2)	0.043(2)	0.006(1)	0.017(1)	0.004(2)
C3	0.038(2)	0.038(2)	0.048(2)	0.004(2)	0.021(2)	0.001(1)
C4	0.043(2)	0.044(2)	0.049(2)	0.006(2)	0.020(2)	0.003(2)
C5	0.081(4)	0.045(3)	0.126(5)	-0.013(3)	0.049(4)	-0.002(3)
O1	0.045(1)	0.057(2)	0.095(2)	-0.001(1)	0.038(1)	-0.008(1)
O2	0.062(2)	0.035(2)	0.088(2)	0.000(1)	0.044(1)	-0.002(2)
C11	0.037(2)	0.039(2)	0.049(2)	0.003(1)	0.020(2)	0.006(2)
C12	0.045(2)	0.089(3)	0.054(3)	0.008(2)	0.017(2)	0.007(2)
C13	0.051(3)	0.098(3)	0.058(3)	0.011(3)	0.009(2)	0.020(3)
C14	0.040(2)	0.055(3)	0.088(4)	0.009(2)	0.007(3)	0.010(3)
C15	0.050(3)	0.083(3)	0.078(3)	0.024(2)	0.019(3)	-0.010(3)
C16	0.050(3)	0.091(3)	0.053(3)	0.021(2)	0.014(2)	0.006(3)

(Continued on next page)

Table 25 continued

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C21	0.033(2)	0.045(2)	0.042(2)	0.002(2)	0.019(2)	0.003(2)
C22	0.064(3)	0.049(3)	0.057(3)	0.011(2)	0.031(2)	0.007(2)
C23	0.086(3)	0.057(3)	0.056(3)	0.014(2)	0.032(2)	0.013(2)
C24	0.076(3)	0.063(3)	0.047(3)	0.002(2)	0.033(2)	0.009(2)
C25	0.075(3)	0.051(3)	0.057(3)	0.002(2)	0.034(2)	-0.001(2)
C26	0.060(2)	0.044(2)	0.050(2)	0.004(2)	0.025(2)	0.002(2)

Table 26Interatomic Distances ($\text{\AA}$)

<u>Atoms</u>	<u>Distance</u>	<u>Atoms</u>	<u>Distance</u>
C1 - C2	1.535 (4)	C23 - C24	1.366 (5)
C2 - C1'	1.532 (4)	C24 - C25	1.366 (5)
C2 - C3	1.526 (4)	C25 - C26	1.385 (5)
C3 - C1'	1.532 (4)	C26 - C21	1.382 (4)
C3 - C4	1.481 (4)	C3 - HB	0.97 (3)
C4 - O1	1.199 (3)	C12 - H12	0.97 (3)
C4 - O2	1.330 (4)	C13 - H13	0.97 (3)
O2 - C5	1.450 (5)	C14 - H14	0.95 (3)
C1 - C11	1.478 (4)	C15 - H15	0.98 (4)
C2 - C21	1.495 (4)	C16 - H16	0.87 (3)
C11 - C12	1.384 (4)	C22 - H22	0.98 (3)
C12 - C13	1.384 (5)	C23 - H23	0.99 (3)
C13 - C14	1.368 (5)	C24 - H24	0.93 (4)
C14 - C15	1.347 (6)	C25 - H25	0.95 (3)
C15 - C16	1.386 (6)	C26 - H26	0.90 (3)
C16 - C11	1.374 (4)	C5 - H51	0.91 (4)
C21 - C22	1.387 (4)	C5 - H52	0.97 (4)
C22 - C23	1.386 (5)	C5 - H53	0.97 (5)

Table 27

Intramolecular Angles

<u>Atoms</u>	<u>Angle</u>	<u>Atoms</u>	<u>Angle</u>
C3' - C1 - C2'	59.7(2)	C2 - C3 - C1'	60.1(2)
C2' - C1 - C2	89.9(2)	C2 - C3 - C4	117.4(3)
C3' - C1 - C11	125.8(3)	C2 - C3 - HB	119(2)
C2' - C1 - C11	134.5(3)	C1' - C3 - HB	120(2)
C11 - C1 - C2	122.6(3)	C4 - C3 - HB	112(2)
C3' - C1 - C2	106.3(2)	C1' - C3 - C4	118.2(3)
C1 - C2 - C1'	90.1(2)	C3 - C4 - O1	126.3(3)
C1 - C2 - C21	123.6(3)	C3 - C4 - O2	110.1(3)
C1 - C2 - C3	106.4(2)	O1 - C4 - O2	123.6(3)
C21 - C2 - C3	123.1(3)	O2 - C5 - H51	108(3)
C21 - C2 - C1'	135.8(3)	O2 - C5 - H52	110(3)
C3 - C2 - C1'	60.1(2)	O2 - C5 - H53	105(3)
H51 - C5 - H53	110(4)	H15 - C15 - C14	124(2)
H51 - C5 - H52	110(4)	H15 - C15 - C16	116(2)
H52 - C5 - H53	113(4)	C14 - C15 - C16	119.9(4)
C1 - C11 - C12	118.6(3)	H16 - C16 - C15	121(2)
C1 - C11 - C16	123.7(3)	H16 - C16 - C11	118(2)
C12 - C11 - C16	117.7(3)	C15 - C16 - C11	121.3(4)
H12 - C12 - C11	120(2)	C2 - C21 - C22	119.6(3)
H12 - C12 - C13	119(2)	C2 - C21 - C26	122.3(3)
C11 - C12 - C13	120.6(3)	C22 - C21 - C26	117.8(3)
H13 - C13 - C12	119(2)	H22 - C22 - C21	117(2)

(Continued on next page)

Table 27 continued

<u>Atoms</u>	<u>Angle</u>	<u>Atoms</u>	<u>Angle</u>
H13 - C13 - C14	121(2)	H22 - C22 - C23	122(2)
C12 - C13 - C14	120.0(4)	C21 - C22 - C23	120.9(4)
H14 - C14 - C13	118(2)	H23 - C23 - C22	116(2)
H14 - C14 - C15	121(2)	H23 - C23 - C24	124(2)
C13 - C14 - C15	120.3(4)	C22 - C23 - C24	120.0(4)
H24 - C24 - C23	117(2)	C24 - C25 - C26	120.0(4)
H24 - C24 - C25	123(2)	H26 - C26 - C25	118(2)
C23 - C24 - C25	120.2(4)	H26 - C26 - C21	121(2)
H25 - C25 - C24	123(2)	C25 - C26 - C21	121.1(4)
H25 - C25 - C26	117(2)		

Table 28

Intramolecular Non-bonded Contacts

Atoms	Distance	Atoms	Distance
C3 - C1	2.451(5)	O1 - O2	2.230(3)
C3 - C2'	2.454(5)	O1 - C21	3.073(4)
C1 - C1'	2.170(6)	O1 - C11'	3.073(4)
C2 - C2'	2.168(6)	O1 - C22	3.218(5)
C4 - C11'	3.123(5)	O1 - C16	3.298(5)
C4 - C21	3.056(5)	C11 - C21	3.425(4)
C3 - C11	3.342(5)	C11' - C21	3.641(5)
C3 - C21'	3.404(5)	C1' - HB	2.18(3)
C3 - C11'	2.679(5)	C2 - HB	2.17(3)
C3 - C21	2.656(5)	C1 - HB	2.58(3)
C3 - O1	2.394(4)	C2 - HB'	2.59(3)
C3 - O2	2.306(4)	C4 - HB	2.05(3)

Table 29

Selected Intermolecular Contacts Less than 4.0 Å

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Symmetry Operation</u>
C5	C12	3.884(8)	$1/2+x, 1/2-y, 1/2+z$
O1	C15	3.302(5)	$1+x, y, z$
O1	C23	3.576(5)	$1/2+x, 1/2-y, 1/2+z$
O2	O2'	3.260(5)	$x, 1+y, z$
O2	C13	3.335(5)	$1/2+x, 1/2-y, 1/2+z$
O2	C12	3.689(5)	$1/2+x, 1/2-y, 1/2+z$
C12	C13	3.828(6)	$-1/2-x, -1/2+y, -1/2-z$
C13	C23	3.635(6)	$-1/2-x, -1/2+y, -1/2-z$
C14	C25	3.625(6)	$-1/2-x, 1/2+y, -1/2-z$
C14	C26	3.701(6)	$-1/2-x, 1/2+y, -1/2-z$
C15	C15'	3.514(10)	$x-1, y, z$
C15	C16'	3.537(7)	$x-1, y, z$
C22	C13	3.769(6)	$-1/2-x, 1/2+y, -1/2-z$
C3	H53'	3.39(5)	$x, 1+y, z$
C5	H24	3.16(4)	$1/2-x, 1/2+y, -1/2-z$
O1	H15	2.43(4)	$1+x, y, z$
O2	H13	2.51(4)	$1/2+x, 1/2-y, 1/2+z$
C12	H23	3.06(4)	$-1/2-x, y-1/2, -1/2-z$
C13	H23	2.83(4)	$-1/2-x, y-1/2, -1/2-z$
C14	H23	2.94(4)	$-1/2-x, y-1/2, -1/2-z$
C16	H15'	2.99(4)	$x-1, y, z$
C24	H52	2.96(4)	$x-1/2, 1/2-y, z-1/2$

(Continued on next page)

Table 29 continued

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Symmetry Operation</u>
C25	H14	3.14(4)	$x-1/2, 1/2-y, z-1/2$
H51	H24	2.47(6)	$1/2-x, 1/2+y, -1/2-z$
H14	H25	2.54(5)	$-1/2-x, 1/2+y, -1/2-z$

Table 30

Geometry of the Cyclopropane Ring

(a) Unfused Systems

Compound Name	C - C	Method	Reference
Cyclopropane	1.510	E.D.	104
Cyclopropyl carbinol	1.514	M.W.	105
Cyclopropane Carboxamide	1.500	X.R.	106
Cis-1,2,3-tricyanocyclopropane	1.518	X.R.	107
Cyclopropyl chloride	1.514	M.W.	108
Bicyclopropyl	1.504	X.R.	109
1,1'-Dimethylbicyclopropyl- 2,2'-dicarboxylate	1.51	X.R.	110
Cis-1,2-diacetonyl-1,2,3,3- tetrachlorocyclopropane	1.50	X.R.	111
Cyclopropane	1.514	R	112
Cyclopropane carboxaldehyde	1.507	E.D.	113

(Continued on next page)

Table 30 continued

(b) Fused Systems

Compound Name	C - C	Method	Reference
2,5-dimethyl-7,7-dicyanonor- caradiene	1.501 (ring junction) 1.557	X.R.	114
6,6-diphenyl-3,3-diethyl- 3-azabicyclo[3.1.0]hexane bromide monohydrate	1.517	X.R.	115
1,5-diphenyltricyclo- [2.1.0.0 ^{2,5}]pent-3-yl p-bromobenzoate	1.44 (junction of cyclopropane rings) 1.53	X.R.	116, 117
Bicyclo[2.1.0]pentane	1.536 (ring junction) 1.507	M.W.	118
Bicyclo[1.1.0]butane	1.498	M.W.	143
1-2,4,5-tetraphenyl-3,6- dicarbomethoxytricyclo [3.1.0.0 ^{2,4}]hexane	1.531	X.R.	This work

X.R. = X-ray

E.D. = Electron Diffraction

M.W. = Microwave

R = Raman

Table 31

Geometry of the Cyclobutane Ring

(a) Unfused Systems

Compound	C - C	Method	Reference
Cyclobutane	1.548	E.D.	119
Cyclobutane	1.558	R.	120
Trans-1,3-cyclobutane-dicarboxylic acid	1.560		91
Trans-1,2-cyclobutane-dicarboxylic acid	1.553 1.517 (between trans substituents)	X.R.	121
Cis-1,2-cyclobutane-dicarboxylic acid	1.554	X.R.	122
Trans-1,2-dyclobutane-dicarboxylic acid-sodium salt (and free acid as solvent of crystallisation)	1.563 (dianion) 1.552 (acid)	X.R.	123
Cis-1,2-dibromo-1,2-dicarbomethoxycyclobutane	1.55	X.R.	124
Trans-1,2-dibromo-1,2-dicarbomethoxycyclobutane	1.56	X.R.	124
Cis-trans-cis-1,2,3,4-tetracyanocyclobutane	1.561 (between cis substituted carbons) 1.547 (between trans substituted carbons)	X.R.	125
Octahydroxycyclobutane	1.563	X.R.	126
Cis-trans-cis-1,2,3,4-cyclobutanetetracarboxylic acid tetramethyl ester	1.572 (between cis substituted carbons) 1.541 (between trans substituted carbons)	X.R.	127

(Continued on next page)

Table 31 continued

Compound	C - C	Method	Reference
2,2,4,4-tetramethyl-cyclobutane-trans-1,3-diol	1.545	X.R.	128
1,1,3,3-tetrafluoro-cyclobutane	1.566	E.D.	129
Cyclobutane carboxylic acid chloride	1.540	E.D.	130
1,2,3,4-tetraphenyl-cyclobutane	1.585 (between cis substituted carbons) 1.555 (between trans substituted carbons)	X.R.	131

(b) Fused Systems

Compound	C - C	Method	Reference
Cubane	1.551	X.R.	132
dl-Photodimer C of 1,3-dimethyl thymine	1.531 (ring junction) 1.574 (inter thymine ring)	X.R.	133
Photodimer E of Thymine	1.547 (ring junction) 1.587 (inter thymine ring)	X.R.	134
Photodimer of cyclopentanone	1.54 (ring junction) 1.59 (inter cyclopentane ring)	X.R.	135
Tricyclo [2.1.0.0 ^{2,5}]-pentane	1.53	X.R.	116, 117

(Continued on next page)

Table 31 continued

Compound	C - C	Method	Reference
Thymine Photodimer	1.540 (ring junction) 1.568 (inter thymine ring)	X.R.	136
Photodimer of 1-methylthymine	1.543 (ring junction) 1.571 (inter thymine ring)	X.R.	137
Bicyclo-[2.1.0]pentane	1.536 (ring junction) 1.565, 1.528, 1.528 average 1.534	M.W.	118
7-endo-chlorobicyclo-[3.2.0]hept-2-ene-6-endo-ol-p-bromobenzoate	1.540 (ring junction) 1.507, 1.537, 1.542 average 1.532	X.R.	138
Trans-Bicyclo[4.2.0]octyl-1-3,5-dinitrobenzoate	1.532 (ring junction) 1.540, 1.547 average 1.544	X.R.	93
3,4:7,8-dibenzo-tricyclo[4.2.0.0 ^{2,5}]-octa-3,7-diene	1.593 (ring junction) 1.559 (inter cyclo-butane rings)	X.R.	139
1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-tricyclo[3.1.0.0 ^{2,4}]-hexane	1.534	X.R.	This Work
Bicyclo[1.1.1]pentane	1.545	E.D.	143
Chlorobicyclo[1.1.1]-pentane	1.536, 1.556	M.W.	144

X.R. = R-Ray, R = Raman, E.D. = Electron Diffraction,

M.W. = Microwave.

Table 32

Least Squares Planes for 1,2,4,5-Tetraphenyl-
3,6-Dicarbomethoxytricyclo[3.1.0.^{2,4}]₆hexane

A. Phenyl Rings

(i) Atoms defining the plane: C11 C12 C13 C14 C15 C16

$$\text{Equation of Plane: } -0.3925X - 0.9194Y + 0.0247Z - 0.5177 = 0$$

Distance of atoms from plane in Å

C11	0.005	C14	0.003
C12	-0.003	C15	0.003
C13	-0.002	C16	-0.007

(ii) Atoms defining the plane. C21 C22 C23 C24 C25
C26

$$\text{Equation of the plane: } 0.8671X + 0.2823Y + 0.4108Z - 0.3045 = 0$$

Distance of atoms from plane in Å

C21	0.008	C24	0.006
C22	-0.003	C25	0.003
C23	-0.005	C26	-0.009

(iii) Atoms defining plane: H12 H13 H14 H15 H16

$$\text{Equation of plane: } -0.3913X - 0.9293Y - 0.0010Z - 0.6105 = 0$$

(Continued on next page)

Table 32 continued

Distance of atoms from plane in Å

H12	-0.020	H15	-0.018
H13	0.026	H16	0.016
H14	-0.004		

(iv) Atoms defining the plane: H22 H23 H24 H25 H26

Equation of plane: $0.8623X + 0.2892Y + 0.4156Z - 0.2793 = 0$

Distance of atoms from plane in Å

H22	0.040	H25	0.010
H23	-0.071	H26	-0.016
H24	0.038		

B. Tricyclic System

(i) Atoms defining the plane: C2 C3 C1'

Equation of plane: $-0.9500X - 0.1976Y + 0.2420Z + 0.7257 = 0$

(ii) Atoms defining the plane: C1 C2 C1' C2'

Equation of plane: $-0.4132X + 0.8212Y + 0.3935Z = 0$

C. Carbomethoxy Group

Atoms defining plane: C4 C5 O1 O2

(Continued on next page)

Table 32 continued

Equation of plane: $0.2706X - 0.1980Y + 0.9421Z -$
 $0.1867 = 0$

Distance of atoms from plane in Å

C4	0.001	O1	-0.0006
C5	0.0008	O2	-0.0009
		C3	-0.0442

Fig. 7

A Perspective View of 1,2,4,5-Tetraphenyl-
3,6-dicarbomethoxytricyclo[3.1.0.0^{2,4}]hexane

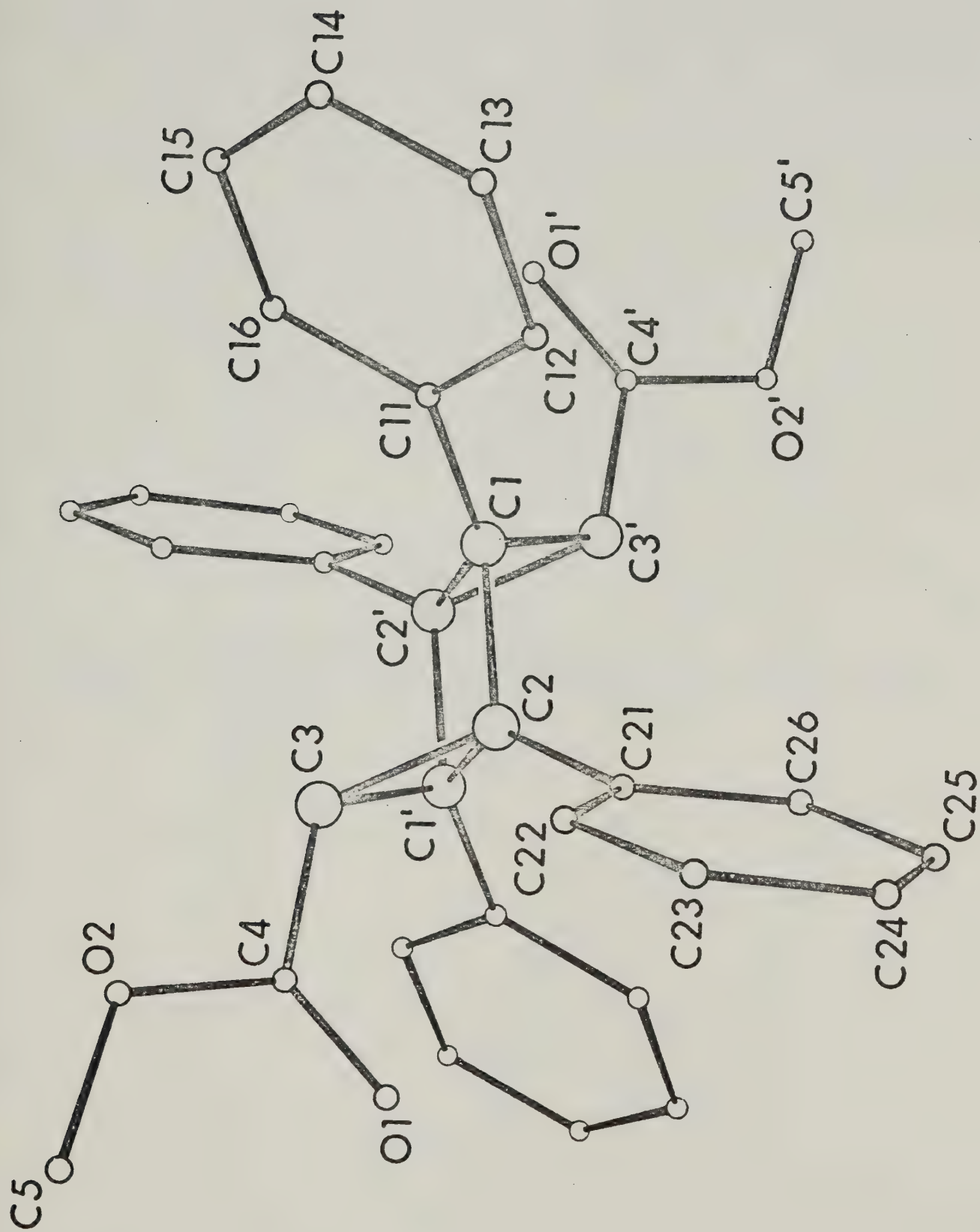


Fig. 8

Contents of the Unit Cell Projected onto the $[a][c]$ Plane.

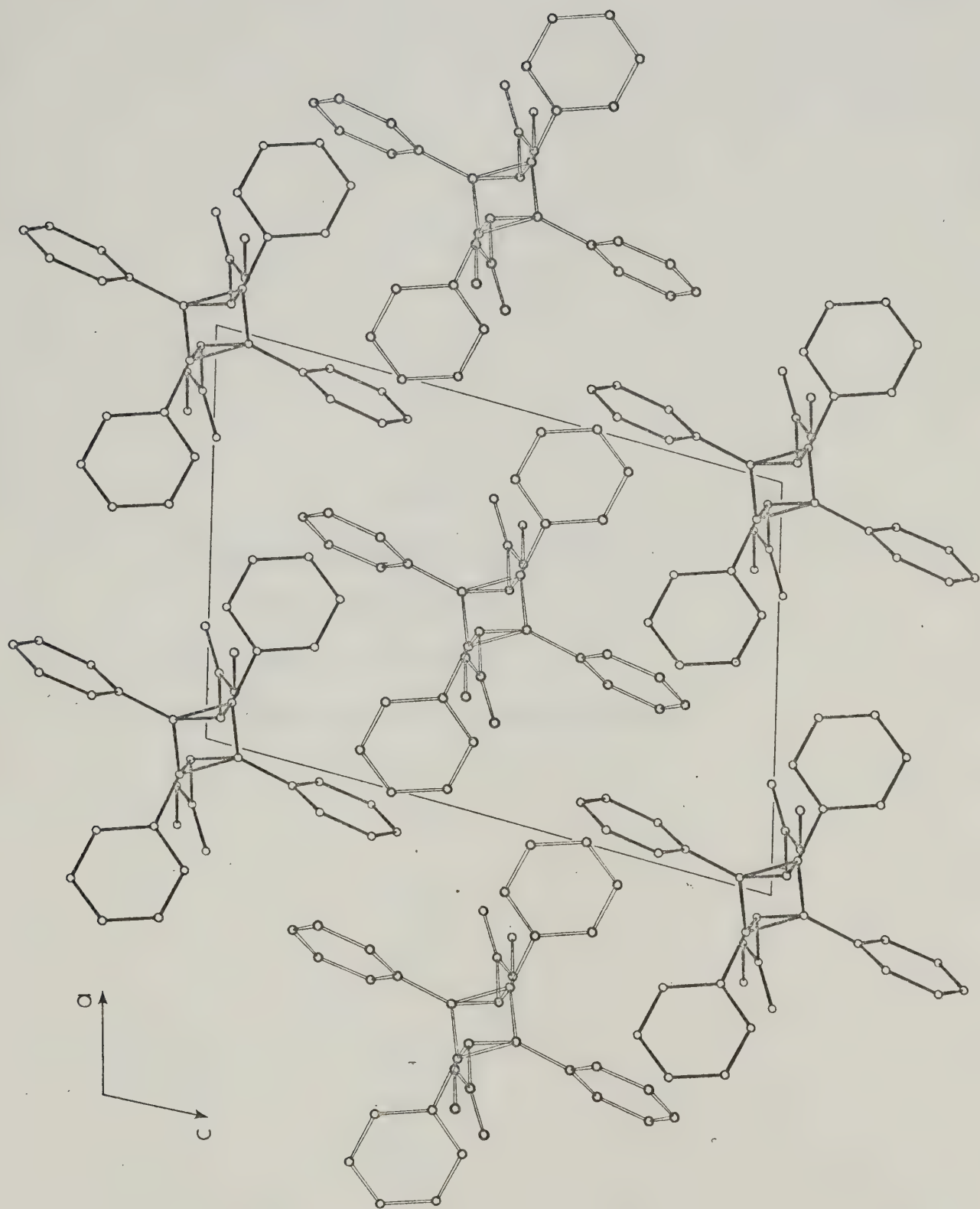
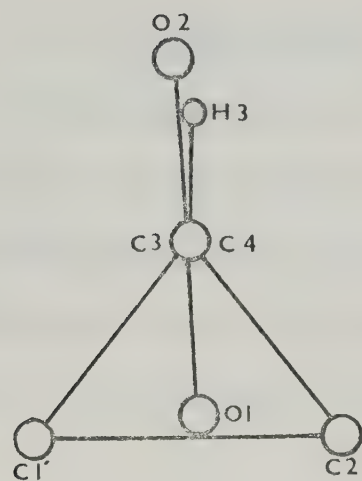


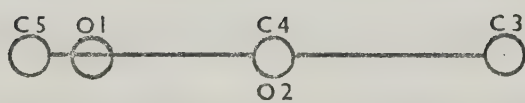
Fig. 9

A Selection of Newman Projections:

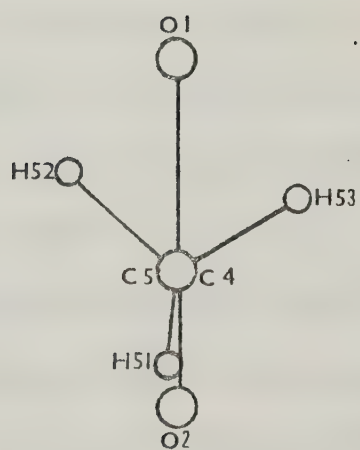
- (a) down C4-C3 bond
- (b) down O2-C4 bond
- (c) down C5....C4 virtual bond



(a)



(b)



(c)

DISCUSSION

1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-tricyclo-[3.1.0.0^{2,4}]hexane crystallises on a crystallographic inversion centre and consequently is in the anti-configuration and has a planar cyclobutane ring. The carbomethoxy groups are in the *exo*-position. A diagram of the molecule is shown in Fig. 8.

The most outstanding detailed structural feature of the molecule is that all bond lengths within the tricyclohexane framework are equal within experimental error and average 1.531 Å. The bond distances in the cyclopropane ring average 1.530 Å and the bond angles within the ring average 60°. The bond lengths are longer than the 1.510 Å bond lengths found in cyclopropane itself¹⁰⁴, and that found in various substituted unfused cyclopropanes (Table 30).

The bond lengths in the cyclobutane ring average 1.534 Å and the ring is planar and square, the bond angles within the ring averaging 90.0°. The bond lengths are shorter than the 1.548 found in cyclobutane itself¹¹⁹ and in substituted unfused cyclobutanes, (Table 31.) The cyclopropane and cyclobutane rings meet at an angle of 109.0°.

The bond distances from the tricyclic system to the substituent phenyl and carbomethoxy groups are all about 0.02 Å shorter than is normally found in unstrained systems. This bond shortening to substituent groups is characteristic of highly strained systems^{114, 140, 141} and has been observed

in many of the compounds listed in Tables 30 and 31.

The angles within the phenyl rings are normal. The angle at the attached carbon atom averages 117.8° and all other angles cluster closely around 120° , with an average value of 120.2° . However, the bond lengths in the phenyl rings range from $1.347 \text{ \AA}$ to $1.389 \text{ \AA}$ with an average value of $1.376 \text{ \AA}$. The variation of bond lengths is systematic. In both rings it is the bonds which are furthest from the tricyclic system which have shortened significantly from accepted values. This bond shortening is undoubtedly due to the effect of thermal motion, probably a libration of the molecule as a whole, which would have the observed effect. The carbon hydrogen distances in the phenyl rings average $0.95 \text{ \AA}$. Both rings are planar within experimental error and the associated hydrogen rings are coplanar with them (Table 32). The plane containing the phenyl ring attached to C2 is perpendicular to the plane of the cyclobutane ring while that attached to C1 is skewed. A similar situation is found in tetraphenyl cyclobutane¹³¹.

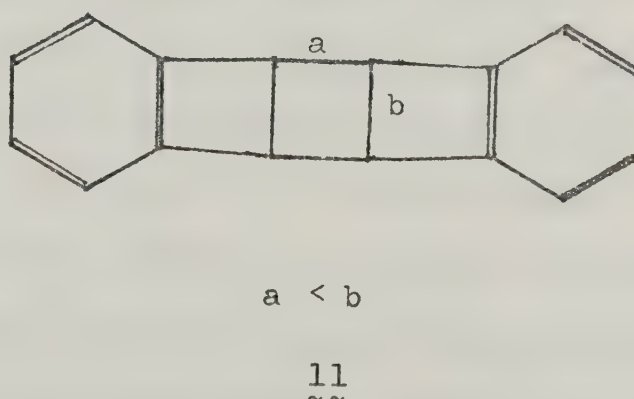
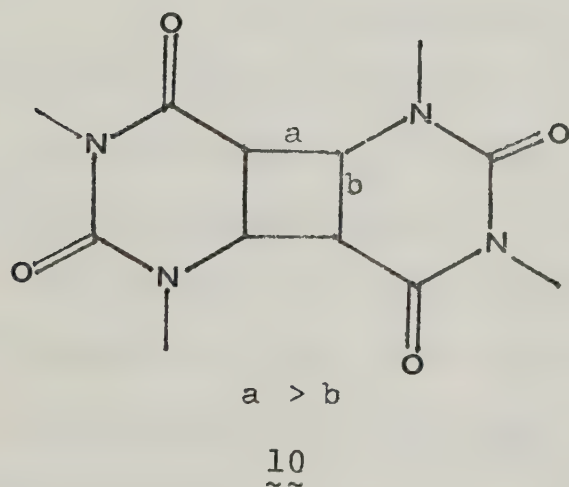
The bond distances and angles within the carbomethoxy group are similar to those found in other compounds (Table 22, Chapter 2). The carbomethoxy group in this compound does not experience such great intramolecular forces as the carbomethoxy group in 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene, as can be seen by the longer C4---C11 and C4---C21 contacts, $3.123 \text{ \AA}$ and $3.056 \text{ \AA}$ respectively, compared with $2.993 \text{ \AA}$ and $2.916 \text{ \AA}$ in the cyclohexadiene deriva-

tive. However, these contacts are still much shorter than the normal Van der Waals contact between two non-bonded carbon atoms. The oxygen contacts with the phenyl groups are all close to or greater than the sum of the Van der Waals radii for carbon and oxygen, the shortest ($3.073 \text{ \AA}$) are the contacts between O1 and the first atom of each phenyl group C21 and C11'. The external angles around C3 are also normal, $C4 - C3 - C2$ is 117.4° and $C4 - C3 - C1'$ is 118.2° , both of which are close to the values found in other substituted cyclopropane rings¹⁰⁶⁻¹⁰⁸, although the $C4 - C3 - HB$ bond angle of 112° is slightly smaller than the 116° average found in these compounds. However the large standard deviation on this angle, makes the difference insignificant. The carbomethoxy group is planar within experimental error. Despite the above, the intramolecular forces would seem to be still great enough to prevent the carbomethoxy group from taking up its preferred orientation with the $C=O$ syn-planar with the $C_\alpha - C_\beta$ bond⁸⁵⁻⁸⁷, in this case the $C3 - C2$ bond. The torsion angle $C2 - C3 - C4 = O1$ is 38.3° , which, being smaller than the 45.9° found in the cyclohexa-1,4-diene derivative, may reflect the lessening of intramolecular nonbonded repulsions in this compound. However Hoffmann and Davidson¹⁴⁶ have pointed out that for a carbomethoxy group attached to a cyclopropane ring the syn-planar arrangement may not be the preferred conformation. They showed that the low lying π^* orbital of the carbonyl can interact with the pseudo- π ring orbital and

this interaction is greatest if the plane containing carbo-methoxy group is perpendicular to the plane of the ring and the C=O is anti-planar with respect to the ring C - H bond, that is if the torsion angle O = C - C - H is 180° . This they termed the bisected conformation. This is exactly the conformation found in this compound. The plane of the carbo-methoxy group is perpendicular to the plane of the cyclopropane ring and the torsional angle O1 - C4 - C3 - HB is 178° . The carbonyl group is also in the preferred syn-planar orientation with respect to the ester methylcarbon^{87,95}, the torsion angle O1 = C - O2 - C5 being 0° . Two other molecules which have this conformation, which Hoffmann and Davidson called the bisected configuration are cyclopropane carboxaldehyde¹¹³ and cyclopropane carboxamide¹⁰⁶. On the other hand, 1,1'-dimethylbicyclopentyl-2,2'-dicarboxylate¹¹⁰, takes up the 'normal' orientation, the O = C - C _{α} - C _{β} torsion angle being 4° .

The cyclobutane ring has equal bond lengths within experimental error which average $1.534 \text{ \AA}$. This is unexpected since in cyclobutane itself the bond length is $1.548 \text{ \AA}$ which is longer than that found in normal paraffins. If the cyclobutane ring is substituted then the bond between cis substituted carbons is even longer^{125,127,131}. In tetraphenylcyclobutane the bond lengths are $1.585 \text{ \AA}$ between the cis substituted carbons, and $1.555 \text{ \AA}$ between the trans substituted carbons¹³¹. Thus the fusion with two cyclopropane rings has drastically affected the geometry of the cyclobutane ring.

In other fused systems containing the cyclobutane ring, the tendency towards longer than normal bond lengths is continued, but the situation is slightly different (Table 31). If the cyclobutane ring is formed by a dimerisation of two unsaturated rings such as two thymine rings 10, then the bridgehead carbon-carbon bond is usually close to normal values, which means that the ring fusion has little effect upon the geometry of the other ring, but the unshared bonds of the cyclobutane ring are elongated, averaging about 1.575 Å in various thymine photodimers^{133,134,136,137} and 1.59 in the photodimer of cyclopentanone¹³⁵. However one structure has been reported in which the bridgehead bonds are significantly longer than the unshared bonds¹³⁹. In 3,4:7,8-di-benzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene 11, the bridgehead carbon-carbon bond is 1.593 Å while the unshared carbon-carbon bond is 1.559 Å. This was rationalised in the following way. In photodimers of thymine, the cyclobutane ring



is fused to two essentially strain free rings, whereas in

3,4:7,8-dibenzotricyclo[4.2.0.0]octa-3,7-diene, the fusing rings are highly strained four membered rings, probably even more strained than the central cyclobutane ring. In this type of system the ring strain and non bonded interactions are relieved by the lengthening of the bridgehead bonds.

If this argument were correct, then one would expect the bridgehead bond in 1,2,4,5-tetraphenyl-3,6-dicarbo-methoxytricyclo[3.1.0.0^{2,4}]hexane to be longer than its unshared cyclobutane bonds, since in this compound, the cyclobutane ring is again fused to two rings which are more strained than it is. However, as has been pointed out all the bonds in this tricyclic system are shorter than are found in other cyclobutane systems. A survey of the literature shows that this shortening of, at least the average, bond length of the cyclobutane ring has been observed in a few other compounds in which the cyclobutane ring exists in a highly strained environment and these will be discussed later.

The cyclopropane ring has bond lengths which are longer than those found in cyclopropane itself, which have been determined by electron diffraction studies to be 1.510 Å. This geometry seems to be little affected by substitution (Table 30). Fusion with other rings, be it with a strained system or a more flexible system, usually results in at least one bond being longer than that found in unfused cyclopropanes, and the average bond length within the ring system tends also

to be longer, except in bicyclo[1.1.0]butane in which all bonds are equal within experimental error and have a value of $1.498 \text{ \AA}$ (Table 30).

In highly strained fused systems, for which structural information is available in the literature, there seems to be a tendency towards shortening of cyclobutane bonds and lengthening of cyclopropane bonds. Thus in one tricyclo[2.1.0.0^{2,5}]-pentane derivative^{116,117} all the bond lengths except one average $1.53 \text{ \AA}$. In a bicyclo[2.1.0]pentane¹¹⁸, the cyclopropane bonds average $1.517 \text{ \AA}$, and the cyclobutane bonds $1.534 \text{ \AA}$. In a bicyclo[3.2.0]heptene derivative, the cyclobutane ring has an average bond length of $1.532 \text{ \AA}$ ¹³⁸.

The microwave structure of bicyclo[2.1.0]pentane is interesting from the point of view of comparison with the structure of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo[3.1.0.0^{2,4}]hexane, since it consists of one cyclopropane ring fused to a planar cyclobutane ring at a dihedral angle of 112.7° while our compound has an extra cyclopropane ring. Here the average bond length in the cyclopropane ring, $1.517 \text{ \AA}$ is slightly longer than that in cyclopropane and the average bond length in the cyclobutane ring is 1.534 , somewhat shorter than the $1.548 \text{ \AA}$ of cyclobutane. Suenram and Harmony argue that since the rings have three and four centre π -like orbitals it is possible for them to relocate the total available electron density around the ring as needed to satisfy geometrical strain or other factors. The observed changes in bond length would

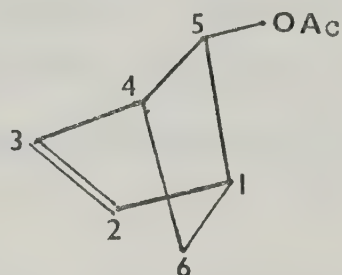
correspond to a small shift of electron density from the cyclopropyl ring to the cyclobutyl ring. The geometry observed in 1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo[3.1.0.0^{2,4}]-hexane would certainly support this delocalisation argument, however as Suenram and Harmony pointed out, such a conclusion must be considered highly speculative, and detailed molecular orbital calculations would be required to see if the predicted electron density provided any supporting evidence for this view. Also arguments of this type neglect the effect of the substituents, which as Hoffman pointed out¹⁴⁵, can greatly affect the geometry of the cyclopropane ring, depending upon whether they have electron donating or electron accepting groups. In a norcardiene derivative¹¹⁴ the lengthening of two bonds in the ring is rationalised on the basis of a delocalisation of electrons from a pseudo π -orbital on the cyclopropane ring into the π^* orbitals of two geminally substituted cyanide groups¹⁴⁵. Since the carbomethoxy group is in the correct position to maximise this type of pseudo π - π^* interaction, the effect of this substituent at least may be important in determining the geometry of the system.

CHAPTER FOUR

Crystal and Molecular Structures of
exo-Tricyclo[3.1.1.0^{2,4}]hept-6-yl p-bromobenzoate.

INTRODUCTION

Exo-tricyclo[3.1.1.0^{2,4}]hept-6-yl acetate were prepared by R. Vukov of this department by the addition of carbene to *exo*-bicyclo[2.1.1]-hex-2-en-5-yl acetate 12. Both *syn* and *anti* isomers were expected since both sides of the double bond



12
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appear equally accessible to the approach of the carbene. However only one major product was obtained from the reaction. Assignment of a *syn* or *anti* configuration to this isomer could not be made on the basis of its n.m.r. spectrum. Consequently the X-ray crystal structure of the p-bromobenzoate derivative was undertaken in order to determine the configuration and also to see if the geometry of the product could provide an explanation of the stereospecificity of the carbene addition. Furthermore this structure determination would provide more information on the geometry of the cyclopropane and cyclobutane rings in highly strained fused systems.

EXPERIMENTAL

A crystal was chosen which was regarded as suitable for photographic work after examination of a Laue photograph. This was used to produce Weissenberg photographs for the $0kl$, $1kl$ and $2kl$ layers and precession photographs for the $hk0$, hkl , and $h0l$, hll layers. The Laue symmetry was found to be $2/m$, and the photographs exhibited the same systematic absences as the tricyclohexane derivative, establishing the space group as $P2_1/n$.

The lattice parameters were obtained by carefully measuring the 2θ values for several reflections, using a PICKER manual four circle diffractometer. A least squares refinement of the cell parameters to give the best fit to the 2θ values yielded the following results: $a = 6.704(1)$; $b = 12.087(1)$; $c = 15.577(2)$; $\beta = 94.12(1)$.

The experimentally observed density of 1.52 gms cm^{-3} , obtained by flotation in aqueous potassium iodide solution, agreed reasonably well with the calculated density of $1.545 \text{ gms cm}^{-3}$, obtained by assuming four molecules of molecular weight 292.9 occupying a cell of volume $1258.96 \text{ \AA}^3$. The density therefore did not require that the molecule occupy a special position within the cell.

Intensity data were collected on a PICKER four circle manual diffractometer. The scan width was 3° with a scan rate of $2^\circ/\text{min}$. The 2θ limit was placed at 90° . A stationary background count was taken on each side of the scan.

In the data reduction process, reflections were re-

jected if $I \leq 0$ or if $I \leq 2\sigma$. 534 of the 1061 measured reflections were rejected in this fashion giving a total of 527 observed reflections.

Six standard reflections were measured at five hour intervals and indicated extensive decomposition. By the end of the data collection the standards had lost some 40% of their original intensity. The decomposition was found to be approximately linear with time, and independent of 2θ . A correction was made by application of a linear scale factor between standards.

The bounding faces of the crystal were tentatively identified as 011 , $0\bar{1}1$, $0\bar{1}\bar{1}$, $01\bar{1}$, $1\bar{1}\bar{1}$ and $\bar{1}00$. The identification of the faces was made difficult because the extensive decomposition obscured the defining edges of the faces. The absorption coefficient was 48.03 cm^{-1} and the maximum dimensions of the crystal were $0.25 \text{ mm} \times 0.07 \text{ mm} \times 0.05 \text{ mm}$.

The data was corrected for absorption and for Lorentz and polarisation effects, and structure amplitudes and standard deviations were calculated.

SOLUTION OF STRUCTURE AND REFINEMENT

The position of the bromine atom in the unit cell was located from a Patterson map and used as input to a structure factor calculation, from which an electron density difference fourier was calculated. The electron density difference fourier gave the positions of the six carbon atoms of the phenyl ring and the carbon and one oxygen of the carboxyl group. A structure factor calculation based on these atoms gave a residual R factor of 0.343 which reduced in one cycle of refinement to 0.323. In these calculations the phenyl ring was included as a rigid body, with C - C bond length of 1.397 Å and a C - C - C angle of 120°.

Another electron density difference fourier was calculated from which five of the atoms of the tricycloheptane system were located. These atoms were included in a structure factor calculation which gave a residual R factor of 0.291 which reduced in one cycle of refinement to 0.259. The temperature factors of two of the atoms in the tricycloheptane system had become quite large and these were removed from subsequent calculations. An electron density difference fourier calculated at this point gave the positions of one more carbon atom of the tricyclic system and the other oxygen of the carboxyl group.

One more cycle of refinement, with what now amounted to fourteen of the seventeen non-hydrogen atoms of the asymmetric unit included in the calculations, reduced R to 0.255. One of these fourteen atoms was again found to have a very

high temperature factor. This atom was removed from the calculations and the R factor fell in two cycles to 0.231. An electron density difference fourier was calculated and this gave the position of the remaining four atoms, which when included in the structure factor calculation caused the refinement to converge in three cycles at $R = 0.140$. Refinement of the bromine atom anisotropically further reduced R to 0.092. On changing from the rigid body to a free atom model, the R factor remained unchanged, but R_2 changed from 0.075 to 0.072. A Hamilton R factor statistical test⁴⁴ showed that the hypothesis that the rigid body model best described the structure could be rejected at the 99.5% confidence level.

The rejection criterion, preventing structure factors for which there was poor agreement between observed and calculated structure amplitude from being used in the least squares refinement, was made more stringent and the R factor fell to 0.089.

Up to this point data which had only been corrected for decomposition and Lorentz and polarisation corrections had been used in the calculations. Now data which had also been corrected for absorption effects was substituted. This had little effect upon the refinement, the R factor falling only slightly to 0.088.

The positions of the hydrogen atoms were calculated assuming a C - H bond length of $1.0 \text{ \AA}$ and, as closely as possible, sp^3 hybridisation at the carbon atoms. These atoms were included in the refinement, with temperature factors one unit

greater than the carbon atom to which they were attached, however, neither their coordinates nor their temperature factors were refined. The refinement then converged in two cycles to $R_1 = 0.080$ and $R_2 = 0.063$.

An electron density difference fourier was computed. This showed rather large peaks around the two oxygen atoms which evidently required anisotropic refinement. Consequently, the hydrogen atoms were removed from the calculations and the refinement repeated with the oxygens anisotropic. The refinement converged at $R_1 = 0.082$ and $R_2 = 0.076$. The positions of the hydrogen atoms were recalculated and when these were included in the calculations the refinement converged to a final $R_1 = 0.072$, $R_2 = 0.055$.

An electron density difference fourier was computed at the end of the refinement and this showed only moderate peaks, the largest, (0.47 electrons $\text{\AA}^{-3}$) occurring near the bromine atom.

RESULTS

The observed and calculated structure amplitudes are listed in Table 33. Table 34 gives the atomic coordinates and thermal parameters of the atoms. Interatomic distances and bond angles are listed in Tables 35 and 36 while nonbonded contacts are shown in Tables 37 and 38. Least squares planes data is presented in Table 40.

A perspective view of the molecule is shown in Fig. 10. A packing diagram in which the contents of the unit cell are projected onto the [b][c] plane is shown in Fig. 11.

TABLE 33

Observed and Calculated Structure Amplitudes (electrons $\times 10$)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H =	0**			-3	-7	160	200	-7	-3	152	156	-7	-7	198	159	-4	-2	197	415
0	2	602	623	-3	-6	144	151	-7	-1	331	356	-7	-6	200	275	-3	-7	173	342
0	4	1126	1130	-3	-5	215	220	-6	-11	204	146	-7	-5	200	203	-3	-4	156	154
0	6	966	931	-3	-4	322	306	-6	-9	172	189	-7	-2	259	233	-3	-3	417	455
0	8	207	184	-3	-3	1005	983	-6	-6	186	170	-7	-1	391	348	-3	-2	335	342
0	10	289	285	-3	-2	269	257	-6	-5	197	213	-6	-10	195	144	-3	-1	195	187
1	1	379	379	-3	-1	478	473	-6	-4	222	203	-6	-7	189	32	-2	-10	182	172
1	3	598	575	-2	-14	186	154	-6	-3	397	413	-6	-6	218	222	-2	-9	182	45
1	4	431	432	-2	-12	258	246	-5	-12	179	125	-6	-4	460	441	-2	-7	427	437
1	5	599	601	-2	-8	701	688	-5	-8	301	329	-5	-9	353	336	-2	-5	393	416
1	6	150	167	-2	-4	883	856	-5	-7	226	178	-5	-8	230	245	-2	-3	270	256
1	7	176	165	-2	-2	787	777	-5	-4	372	367	-5	-5	282	288	-2	-1	663	671
1	8	177	195	-2	-1	507	480	-5	-3	420	416	-5	-3	300	290	-1	-10	245	270
1	10	154	138	-1	-10	260	275	-5	-2	145	38	-5	-2	275	275	-1	-7	312	275
1	11	200	217	-1	-9	210	238	-5	-1	437	411	-5	-1	230	200	-1	-6	208	175
1	12	153	177	-1	-7	423	436	-4	-8	223	263	-4	-11	217	217	-1	-4	330	316
1	13	155	158	-1	-6	353	351	-4	-6	465	488	-4	-3	546	534	-1	-3	390	418
2	0	223	222	-1	-5	197	226	-4	-2	609	609	-4	-2	200	164	-1	-2	266	256
2	1	815	830	-1	-4	323	292	-3	-11	150	228	-4	-1	385	366	0	-8	324	352
2	2	941	906	-1	-3	398	368	-3	-10	279	303	-3	-9	204	208	0	-4	638	639
2	3	1007	972	-1	-2	910	825	-3	-7	348	322	-3	-8	193	185	0	0	324	295
2	4	137	134	0	-11	328	330	-3	-6	305	320	-3	-6	348	358	0	2	556	578
2	7	817	819	0	-9	171	179	-3	-5	863	833	-3	-5	400	416	0	4	194	186
2	8	194	165	0	-7	245	243	-3	-4	713	699	-3	-2	562	513	0	6	344	332
2	9	253	221	0	-5	1110	1060	-3	-1	560	585	-3	-1	401	417	0	8	233	236
2	11	228	225	0	-3	160	107	-2	-12	260	234	-2	-12	175	102	1	0	564	574
2	13	170	140	0	-1	795	804	-2	-9	391	427	-2	-10	381	431	1	1	282	302
3	1	1092	1102	0	1	478	525	-2	-6	369	357	-2	-6	547	510	1	4	240	253
3	2	405	401	0	3	2075	2064	-2	-5	727	713	-2	-4	379	391	1	5	180	83
3	3	538	532	0	5	698	706	-2	-3	529	546	-2	-3	546	521	1	7	212	161
3	5	406	368	0	7	144	179	-1	-11	301	340	-1	-9	330	378	1	8	220	234
3	6	407	393	0	9	735	763	-1	-10	214	208	-1	-8	237	249	2	0	140	101
3	7	148	132	0	11	163	103	-1	-8	450	454	-1	-6	528	455	2	1	242	346
3	8	355	340	1	0	92	88	-1	-7	565	564	-1	-5	555	509	2	3	381	391
3	9	144	168	1	1	235	250	-1	-5	467	467	-1	-4	394	370	2	5	210	208
3	11	143	88	1	2	685	653	-1	-4	353	359	-1	-3	685	637	2	9	220	220
4	0	594	605	1	3	632	628	-1	-3	612	605	-1	-2	848	834	3	0	217	226
4	1	176	181	1	4	156	179	-1	-2	313	317	0	-11	270	221	3	1	210	198
4	2	253	242	1	5	383	376	-1	-1	399	408	0	-9	349	367	3	4	258	279
4	3	284	302	1	7	336	350	0	-12	308	358	0	-7	492	504	3	7	238	238
4	4	503	511	1	8	319	302	0	-10	240	271	0	-5	598	515	4	2	360	358
4	6	480	475	1	9	167	82	0	-8	276	295	0	-3	833	850	4	6	227	187
4	8	166	145	2	0	626	646	0	-6	646	655	0	-1	623	633	5	0	420	420
4	10	307	287	2	1	1194	1201	0	-4	557	541	0	1	417	426	5	1	303	323
5	1	532	537	2	2	1923	1908	0	-2	1309	1280	0	3	622	624	5	4	225	159
5	2	381	403	2	3	514	510	0	0	471	479	0	7	492	499	5	5	152	110
5	4	140	134	2	4	618	624	0	2	693	677	0	9	185	175	5	6	188	94
5	5	483	480	2	5	240	257	0	4	719	787	0	11	171	156	6	3	156	94
5	6	146	182	2	6	634	649	0	8	367	358	1	0	155	165	6	4	163	134
5	8	243	256	2	8	509	537	0	10	172	122	1	1	576	597	6	5	190	218
5	9	147	183	2	10	220	211	0	12	180	185	1	2	174	159	7	1	145	171
6	1	376	368	2	12	162	148	1	0	350	364	1	3	312	298	7	3	212	205
6	3	430	431	3	0	298	403	1	2	586	580	1	5	501	540	7	4	158	121
6	4	321	330	3	1	1064	1079	1	3	594	582	1	6	168	99	9	0	164	136
6	7	222	217	3	2	328	328	1	4	135	95	1	8	197	175	9	2	128	13
6	11	167	126	3	3	740	736	1	5	331	331	1	11	177	115	**H =	5****		
7	1	213	228	3	4	418	451	1	6	349	377	2	0	736	758	-6	-3	178	21
7	2	277	301	3	5	328	332	1	7	203	166	2	2	269	251	-5	-5	320	296
7	3	121	27	3	7	174	170	1	9	293	284	2	4	540	514	-5	-4	229	200
7	4	140	122	3	8	153	155	1	10	191	151	2	5	233	207	-4	-5	346	344
7	8	207	183	3	12	158	73	1	12	158	92	2	6	447	469	-4	-2	204	90
7	9	237	246	4	1	475	485	2	1	784	790	2	10	260	238	-4	-1	388	411
8	0	278	274	4	2	429	442	2	2	193	165	3	0	165	169	-3	-8	197	250
8	1	175	171	4	3	380	392	2	5	808	795	3	1	329	353	-3	-7	193	198
8	2	299	294	4	4	155	205	2	7	269	369	3	2	334	338	-3	-2	200	178
8	3	245	266	4	5	418	412	2	11	314	331	3	5	147	146	-3	-1	195	175
8	4	318	324	4	6	334	331	3	0	536	569	3	6	264	255	-2	-6	297	331
8	5	135	78	4	7	130	87	3	1	304	290	3	7	179	90	-2	-2	456	451
8	6	234	185	4	9	264	269	3	3	296	286	3	9	195	120	-1	-7	193	207
8	8	152	88	5	0	242	250	3	4	297	290	4	1	261	261	-1	-5	224	261
9	1	224	188	5	1	540	517	3	6	525	534	4	2	189	255	-1	-4	302	285
9	2	165	173	5	2	186	221	3	7	151	171	4	3	322	301	-1	-1	375	399
9	7	186	192	5	3	324	342	3	9	147	128	4	4	203	88	0	-9	328	266
10	0	139	190	5	4	383	369	3	10	183	171	4	7	314	303	0	-5	424	414
10	5	145	108	5	5	187	143	4	0	458	472	4	9	190	151	0	-3	313	308
11	5	163	139	5	6	126	65	4	1	321	318	5	1	268	257	0	1	394	373
H =	1**			5	7	300	285	4	2	615	628	5	2	386	386	0	3	242	202
-9	-3	206	178	5	8	202	229	4	3	202	177	5	6	219	282	0	5	297	264
-8	-5	211	172	5	9	144	39	4	4	970	970	6	0	285	310	1	0	327	335
-7	-10	163	148	6	0	569	583	4	5	354	372	6	2	233	189	1	2	173	163
-7	-6	346	335	6	1	227	257	4	7	304	313	6	4	149	187	1	3	252	203
-7	-5	154	164	6	2	614	608	4	8	443	442	6	6	299	269	1	5	185	142
-7	-3	202	206	6	4	119	57	4	10	263	290	7	2	236	250	2	0	263	197
-6	-8	170	155	6	5	280	281	5	0	122	104	7	3	189	133	2	2	240	246
-6	-6	191	204	6	6	452	473	5	3	537	552	7	5	250	2				

Table 34

Atomic Coordinates and Temperature Factors

Atom	x	y	z	B
Br	0.0798 (3)	0.1298 (2)	0.1017 (2)	7.3*
O1	0.816 (2)	0.193 (1)	-0.178 (1)	7.8*
O2	0.891 (2)	0.330 (1)	-0.083 (1)	6.4*
C1	1.005 (3)	0.433 (1)	-0.209 (1)	5.7 (5)
C2	1.219 (3)	0.443 (2)	-0.242 (1)	7.0 (6)
C3	1.325 (3)	0.551 (2)	-0.226 (1)	6.5 (5)
C4	1.338 (3)	0.470 (2)	-0.157 (2)	6.9 (5)
C5	1.158 (3)	0.466 (1)	-0.096 (1)	5.5 (5)
C6	1.058 (2)	0.358 (2)	-0.132 (1)	4.8 (4)
C7	0.989 (3)	0.527 (1)	-0.145 (1)	4.9 (5)
C8	0.785 (3)	0.244 (2)	-0.112 (2)	5.0 (5)
C9	0.617 (2)	0.216 (1)	-0.056 (1)	4.0 (4)
C10	0.485 (2)	0.132 (2)	-0.086 (1)	5.5 (4)
C11	0.326 (2)	0.105 (2)	-0.037 (1)	4.9 (5)
C12	0.298 (2)	0.163 (1)	0.037 (1)	4.8 (5)
C13	0.426 (3)	0.247 (1)	0.067 (1)	4.3 (4)
C14	0.591 (3)	0.272 (1)	0.017 (1)	4.4 (4)

*These are equivalent B's corresponding to the following anisotropic parameters:

(Continued on next page)

Table 34 continued

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.061(1)	0.121(2)	0.099(2)	-0.036(2)	0.018(1)	0.021(3)
O1	0.088(11)	0.087(11)	0.129(14)	-0.031(8)	0.061(10)	-0.050(10)
O2	0.073(10)	0.080(11)	0.096(12)	-0.042(9)	0.035(9)	0.001(7)

Table 34 continued

Calculated Hydrogen Positions

Atom	x	y	z	B
H1	0.881	0.413	-0.249	7.4
H2	1.271	0.385	-0.282	8.5
H31	1.241	0.623	-0.220	7.6
H32	1.442	0.575	-0.260	7.6
H4	1.471	0.429	-0.140	7.7
H5	1.186	0.477	-0.032	6.4
H6	1.159	0.296	-0.143	6.0
H71	0.861	0.536	-0.113	6.2
H72	1.022	0.605	-0.166	6.2
H10	0.512	0.092	-0.142	7.0
H11	0.232	0.043	-0.055	5.4
H13	0.401	0.289	0.121	5.8
H14	0.687	0.337	0.036	6.0

Table 35

Interatomic Distances

<u>Atoms</u>	<u>Distance</u>
BR - C12	1.88 (2)
C9 - C10	1.40 (2)
C10 - C11	1.39 (2)
C11 - C12	1.37 (2)
C12 - C13	1.39 (2)
C13 - C14	1.42 (2)
C14 - C9	1.36 (2)
C8 - C9	1.51 (2)
C8 - O1	1.23 (2)
C8 - O2	1.32 (2)
O2 - C6	1.44 (2)
C1 - C2	1.56 (2)
C1 - C6	1.52 (2)
C1 - C7	1.52 (2)
C2 - C3	1.50 (2)
C2 - C4	1.53 (3)
C3 - C4	1.46 (2)
C4 - C5	1.59 (2)
C5 - C6	1.54 (2)
C5 - C7	1.52 (2)

Table 36

Intramolecular Angles

<u>Atoms</u>	<u>Angle</u>	<u>Atoms</u>	<u>Angle</u>
C1 - C6 - C5	82.0 (14)	C1 - C6 - O2	114.1 (15)
C6 - C5 - C7	86.5 (13)	C5 - C6 - O2	110.4 (15)
C5 - C7 - C1	82.9 (13)	O2 - C8 - O1	123.6 (21)
C7 - C1 - C6	87.2 (14)	O2 - C8 - C9	113.0 (21)
		O1 - C8 - C9	123.4 (22)
C7 - C1 - C2	105.3 (15)		
C6 - C1 - C2	98.0 (15)	C8 - C9 - C10	116.8 (19)
C7 - C5 - C4	104.8 (15)	C8 - C9 - C14	121.5 (19)
C6 - C5 - C4	98.1 (15)	C14 - C9 - C10	121.7 (18)
C1 - C2 - C3	117.1 (17)	C9 - C10 - C11	118.1 (19)
C5 - C4 - C3	117.1 (17)	C10 - C11 - C12	120.3 (18)
C1 - C2 - C4	99.9 (16)	C11 - C12 - C13	122.1 (17)
C5 - C4 - C2	97.7 (15)	C12 - C13 - C14	117.5 (16)
		C13 - C14 - C9	120.3 (17)
C4 - C2 - C3	57.5 (12)		
C2 - C3 - C4	62.3 (12)	C13 - C12 - Br	117.6 (15)
C3 - C4 - C2	60.2 (12)	C11 - C12 - Br	120.3 (14)

Table 37

Intramolecular Non-Bonded Contacts

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
C1	C5	2.01(3)	BR	C11	2.83(2)
C6	C7	2.10(2)	BR	C13	2.81(2)
C6	C2	2.33(3)	O1	O2	2.25(2)
C6	C4	2.37(3)	O1	C6	2.64(2)
C7	C2	2.45(3)	O1	C1	3.21(2)
C7	C4	2.46(3)	O1	C10	2.83(3)
C1	C4	2.36(3)	O2	C5	2.45(2)
C5	C2	2.35(3)	O2	C1	2.48(2)
C6	C3	3.34(3)	O2	C7	2.70(2)
C7	C3	2.68(3)	O2	C14	2.73(2)
C5	C3	2.60(3)	C6	C8	2.33(3)
C1	C3	2.61(3)	H31	H72	1.76

(from calculated
positions)

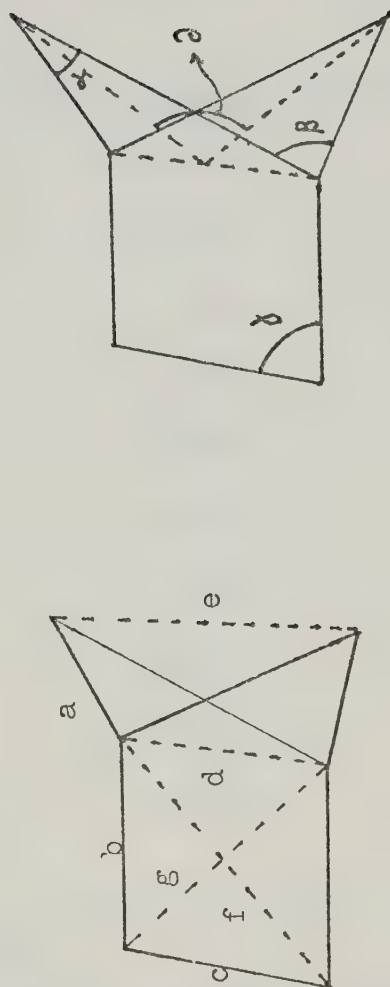
Table 38

Intermolecular Contacts

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Symmetry Operation</u>
BR	C2	3.67 (2)	$x-1 \frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$
BR	C14	3.85 (2)	$x-1, y, z$
BR	O2	3.91 (2)	$x-1, y, z$
BR	C3	3.94 (2)	$x-1 \frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$
O1	C3	3.39 (2)	$x+1 \frac{1}{2}, \frac{1}{2}+y, \frac{1}{2}-z$
O1	C7	3.87 (2)	$x+1, y, z$
O2	C5	3.76 (2)	$2-x, 1-y, -z$
O2	C12	3.78 (2)	$1+x, y, z$
C2	C10	3.71 (2)	$1 \frac{1}{2}-x, \frac{1}{2}+y, -z-\frac{1}{2}$
C3	C10	3.60 (2)	$1 \frac{1}{2}-x, \frac{1}{2}+y, -z-\frac{1}{2}$
C5	C14	3.76 (2)	$2-x, 1-y, -z$
C6	C11	3.79 (2)	$1+x, y, z$
C6	C12	3.80 (2)	$1+x, y, z$
C10	C11	3.62 (2)	$1-x, -y, -z$
C11	C11	3.59 (2)	$1-x, -y, -z$

Table 39

Comparison of Bicyclo[2.1.1]hexane Geometries



Ref.	a	b	c	d	e	f	g	α	β	γ	ϑ
147	1.544	1.565	1.513	2.172	1.946	2.381	2.395	89.4	78.2	102.1	125.0
148	1.547	1.537	1.537	2.098	2.057	2.374	2.364	85.4	83.3	100.5	129.5
This Work (average values)	1.53	1.575	1.53	2.01	2.10	2.40	2.36	82.1	86.8	98.8	132.1

Table 40

Least Squares Planes and Dihedral Angles

(i) Phenyl Ring

Atoms defining plane: C9, C10, C11, C12, C13, C14

Equation of Plane:

$$0.5286X - 0.6702Y + 0.5210Z - 0.0151 = 0$$

Distance of atoms from plane ($\text{\AA}$):

C9	-0.001
C10	-0.007
C11	0.011
C12	-0.006
C13	-0.002
C14	0.005
BR	-0.020
C8	-0.047
O1	-0.027
O2	-0.158

(ii) Plane A

Atoms defining plane: C5, C6, C1

Equation of plane:

$$-0.8818X + 0.2619Y + 0.3921Z + 6.0507 = 0$$

(Continued on next page)

Table 40 continued

(iii) Plane B

Atoms defining plane: C5, C1, C7

Equation of plane:

$$-0.7030X - 0.5251Y + 0.4796Z + 9.2034 = 0$$

(iv) Plane C

Atoms defining plane: C5, C1, C2, C4

Equation of plane:

$$0.1428X - 0.9777Y + 0.1537Z + 4.6116 = 0$$

Distance of atoms from plane ($\text{\AA}$)

C5 0.004

C1 -0.004

C2 0.006

C4 -0.006

(v) Plane D

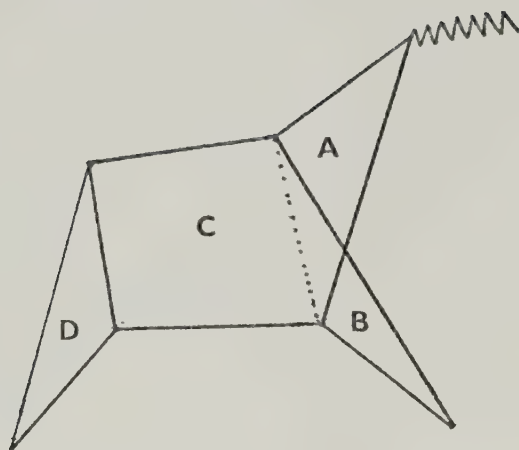
Atoms defining plane: C2, C3, C4

Equation of plane:

$$-0.8483X + 0.3878Y + 0.3605Z + 6.4368 = 0$$

(Continued on next page)

Table 40 continued



Plane 1	Plane 2	Dihedral Angle
A	B	132.1°
A	C	108.8°
B	C	119.1°
C	D	116.4°

Fig. 10

A Perspective View of
exo-Tricyclo[3.1.1.0^{2,4}]-6-yl-p-bromobenzoate.

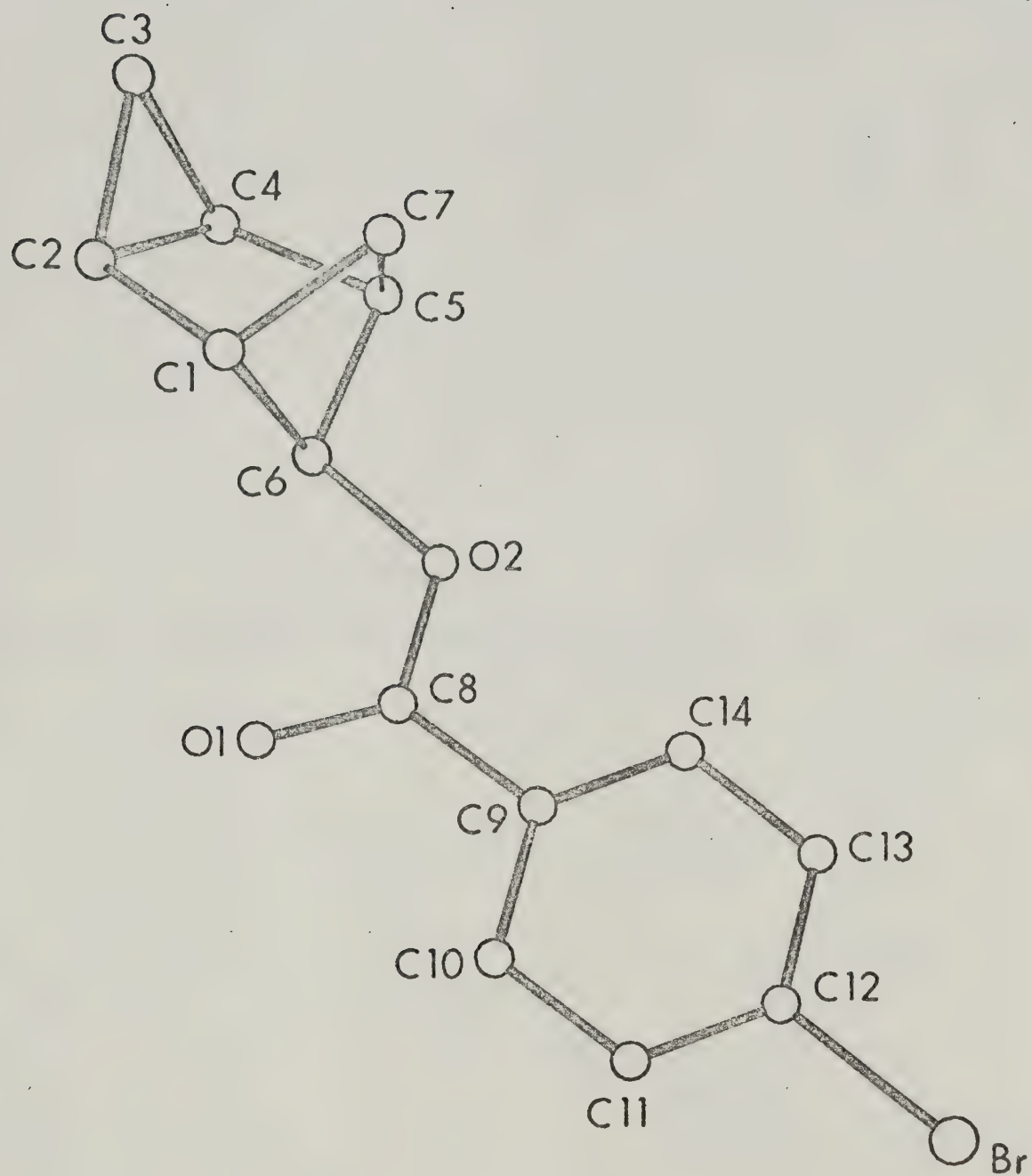
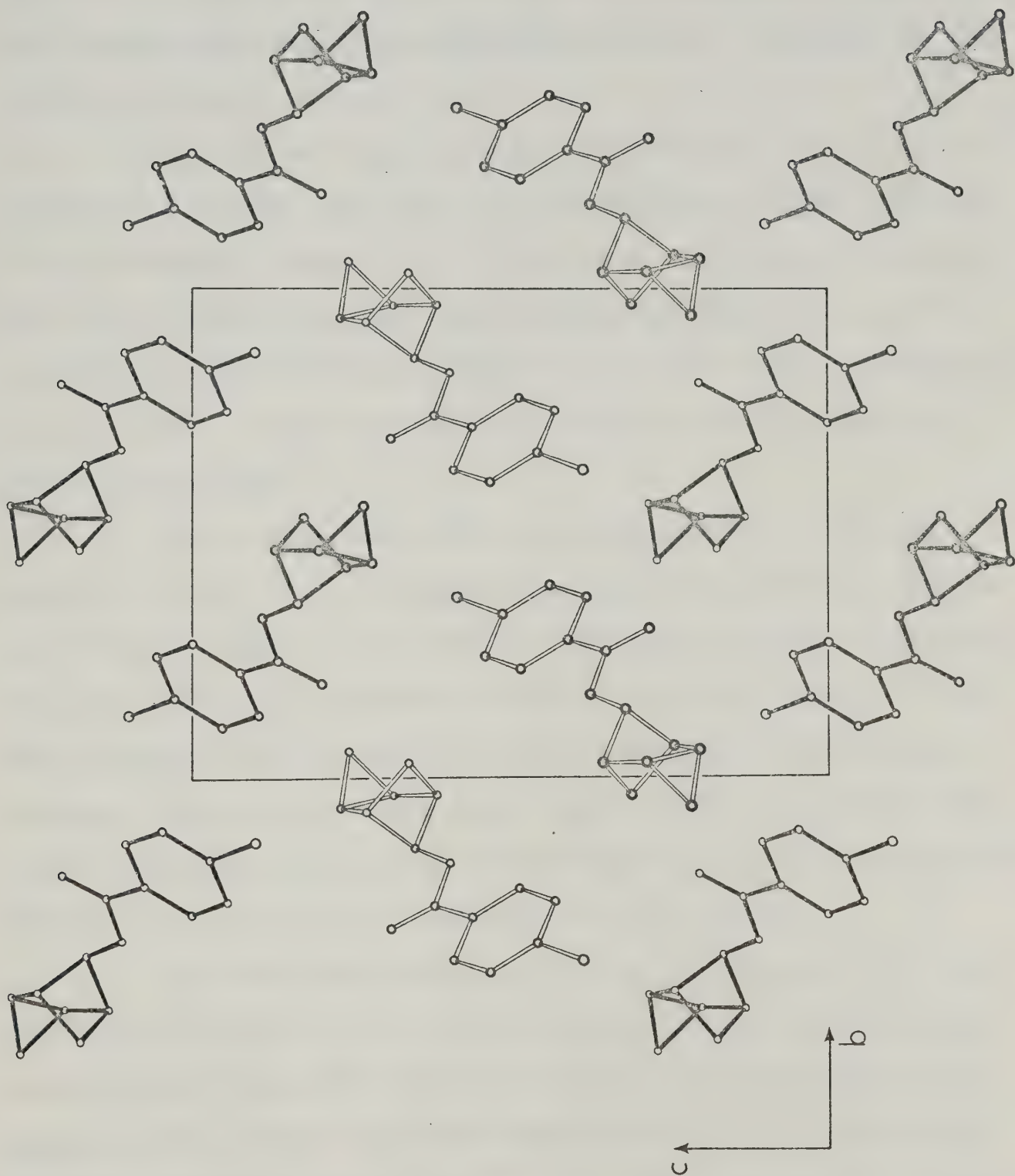


Fig. 11

Contents of the Unit Cell Projected onto the $[b][c]$ Plane



DISCUSSION

Tricyclo[3.1.1.0^{2,4}]hept-6-yl-p-bromobenzoate crystallises with the cyclopropane ring *anti* relative to the bridgehead bearing the exo-p-bromobenzoate group. A diagram of the molecule is shown in Fig. 10.

The rather large standard deviations for the bond lengths and angles does not allow discussion of the geometry of the molecule beyond that of the gross structural features. The cyclopropane ring has an average bond length of 1.50 Å, the bridgehead bond being longest at 1.53 Å. The average bond angle is 60°. These values are similar to those found in cyclopropane itself.

The cyclobutane ring is puckered with a dihedral angle of 132.1°. The average bond length within the ring is 1.53 Å which would agree with the observation that cyclobutane bond lengths are shortened in highly strained systems. However, because of the large standard deviations in the bond lengths, this value is not significantly different from that found in cyclobutane itself. The angles within the cyclobutane ring are 87° at C1 and C5 and 82.5° at C6 and C7.

Part of the molecule consists of a bicyclo[2.1.1]hexane entity, and it is interesting to compare the geometry found in this structure with that found for bicyclo[2.1.1]hexane itself, which has been determined by two independent electron diffraction studies^{147,148}. This comparison is summarised in Table 39. As can be seen from the table this structure does not differ significantly from either of the

other two structures, but most of the dimensions and angles are closer to Dallinga and Toneman's structure¹⁴⁸. Apart from the sizeable errors in the geometry of the system, the presence of the cyclopropane ring undoubtedly has an effect upon the system, especially upon the bond lengths and angles around C2 and C4. Thus it would be meaningless to use this structure to try to resolve the conflict between the two electron diffraction results.

The phenyl ring of the p-bromobenzoate group is planar within experimental error and the bromine atom lies in this plane (Table 40). The C - Br bond length is 1.88 Å and the average C - C bond length in the ring is 1.39 Å. The average bond angle is 120°. The carboxyl group has a normal geometry (see Table 22 p 107). The overall geometry of the p-bromobenzoate group is similar to that found in other structures^{138,149}.

The anti isomer was the only product in the addition of carbene to exo-bicyclo[2.1.1]hex-2-ene-5-yl acetate. It has been suggested that the hydrogen at C5 may exert some steric control on the reaction, if intramolecular forces between the acetate group and the hydrogens on C6 of the bicyclohexene derivative forced C5 closer to the double bond than C6¹⁵⁰. The hydrogen on C5 would then sit further over the double bond than the hydrogen on C6, hindering the approach of the carbene from that side. There is some structural evidence to support this view.

The plane formed by C1, C5, C2 and C4 (plane C) makes a dihedral angle of 108.8° with the plane defined by

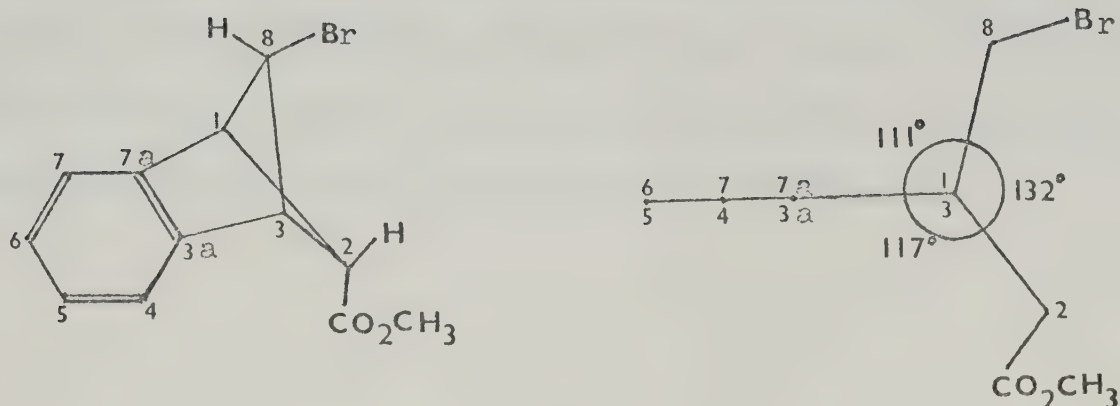
C1, C5 and C6 (plane A) but a much greater angle 119.1° with the plane defined by C1, C5 and C7 (plane B). It also is inclined at 116.4° to the cyclopropane ring (plane D). Because of the difference in dihedral angle, C6 sits closer to the C2 - C4 bond (which would be the C2 - C3 double bond in bicyclo[2.1.1]hexene) than C7. This is further evidenced by the difference in C2---C6, C4---C6 and C2---7 and C4---C7 non-bonded contacts. Those between C2, C4 and C6 average $2.35 \text{ \AA}$ shorter than the corresponding contacts with C7 which average $2.45 \text{ \AA}$. Also angles C7 - C1 - C2 and C7 - C5 - C4 are greater than angles C6 - C1 - C2 and C6 - C5 - C4. Those angles involving C7 average 105° while those involving C6 average 98° .

The question remains as to whether the difference in dihedral angle is a result of intramolecular forces between the p-bromobenzoate substituent at C6, and C7, forcing C6 closer to the C2 - C4 bond, or whether it is the result of intramolecular forces between the hydrogens attached to C3, and those on C7, forcing C7 away from the C2 - C4 bond. If it is the former, then the same situation would exist in the parent olefin and this could explain the formation of only one product in the reaction with carbene. The intramolecular forces in question are those between C7 and O2 between which there is the very short distance of $2.70 \text{ \AA}$, and those between H31 and H72 which have been calculated to be only $1.76 \text{ \AA}$ apart. C3 and C7 are only $2.68 \text{ \AA}$ apart too, an extremely short non-bonded contact.

There is some evidence, although most of it indirect, to support the proposition that C6 is being forced closer to C2 - C4 bond, which in turn means that C5 in the bicycloolefine is being forced closer to the double bond.

To reduce the repulsive interaction between C3 and C7, either plane D can move back, widening the dihedral angle between D and C from its preferred value, or plane B can widen its dihedral angle with C, or both can occur. Plane D makes a dihedral angle with plane C of 116.4° which is wider than the 109.0° found in anti-1,2,4,5-tetraphenyl-3,6-dicarbo-methoxytricyclo[3.1.0.0^{2,4}]hexane. The dihedral angle between B and C is 119.1° . In bicyclohexane itself, the average value for this angle obtained from the two electron diffraction studies is 116.25° . In bicyclohexene¹⁴⁷, this angle is 118.25° . Thus it would seem that the repulsive forces are reduced by widening the dihedral angle between D and C to 116.4° from a preferred 109.0° and possibly by lengthening the bonds between C1 and C2, and C4 and C5 ($1.575 \text{ \AA}$ average). Also the dihedral angle between plane A and plane C is reduced to 108.8° from a preferred angle of 117° . Plane B is relatively unaffected.

The structure of a related compound, 8-exo-bromo-1,3-methanoindane-2-endo-carboxylate 13 has been determined¹⁵¹. In this compound there are no repulsions of the type encountered between C3 and C7 in the tricyclo[3.1.1.0^{2,4}]heptane derivative. The dihedral angles then depend upon the substituents at the bridgehead. The bromine in the exo compound is only



13
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3.15 Å from C2 while the sum of the Van der Waals radii for bromine and carbon is 3.65 Å. This is similar to the type of interaction between O2 and C7 in the tricycloheptane derivative. The dihedral angle between the planes which correspond to A and C in the tricycloheptane compound is 111° while that which would correspond to the angle between B and C is 117°. Thus the same pattern is observed with or without the presence of the cyclopropane ring, so that these angles are influenced mainly by the substituents at the bridgehead positions.

By extrapolation then it would appear that C5 in exo-bicyclo[2.1.1]hex-2-en-5-yl acetate will be closer to the C2 - C4 bond and the hydrogen attached to it may sterically interfere with the formation of a syn isomer of tricyclo-[3.1.1.0^{2,4}]hept-6-yl acetate.

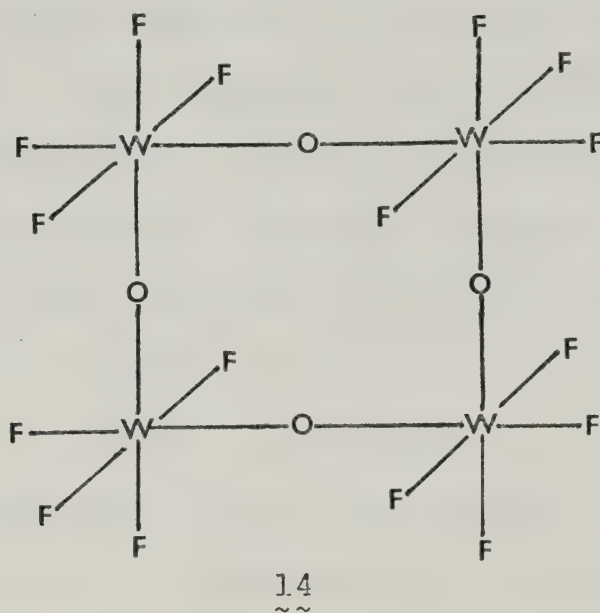
A packing diagram of the molecule is shown in Fig. 11, in which the contents of the unit cell have been projected on to the [b][c] plane. Intermolecular contacts are listed in Table 38. None of these are less than the sum of the

Van der Waals radii of the two atoms concerned. The closest packing occurs in the direction of the a axis. Other close contacts occur between molecules related by the n glide and separated by two unit cells in the a direction.

APPENDIX

The Structure of Tungsten Oxide Tetrafluoride.

As part of a general structural investigation of fluorides and oxide tetrafluorides, the solid state structure of tungsten oxide tetrafluoride was carried out by Edwards and Jones¹⁵². The reported structure consisted of a tetrameric unit with idealised symmetry D_{4h} 14.



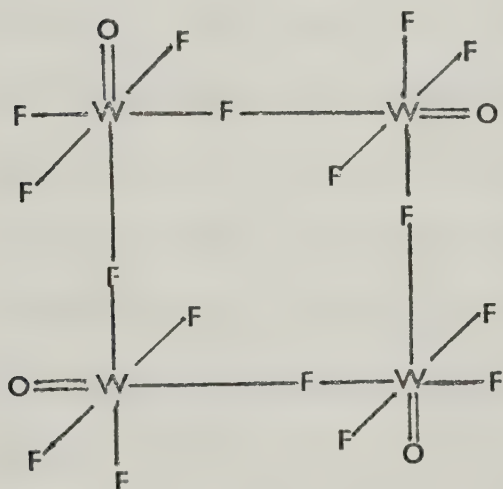
The assignment of the oxygen atoms to the bridging positions was based on the symmetry requirements of the space group and the stoichiometry of the compound. This assignment assumed an ordered structure, and no disordered structures with fluorine atoms in the bridging positions were tested.

The oxygen bridged structure has been criticized on the basis of the infrared and Raman spectra of the tetramer in the solid state^{153,154}. On the basis of their structure determination, Edwards and Jones had assigned a band at 1050 cm^{-1} to a terminal W - F stretching frequency. Beattie and co-workers found this untenable, since in NbF_5 and TaF_5 , which are structurally similar to WOF_4 , no fundamental higher than

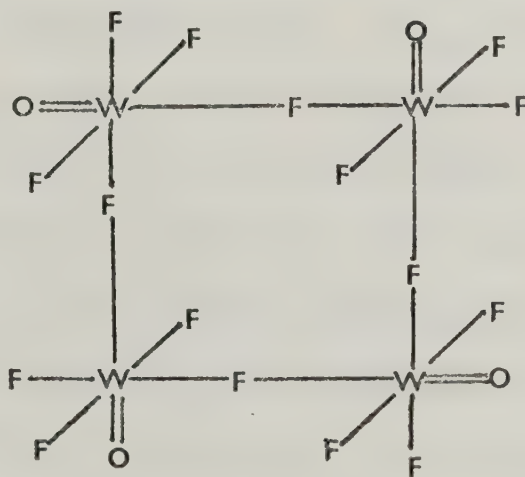
766 cm^{-1} is observed, and so assigned the band at 1050 cm^{-1} to either a terminal or bridging oxygen mode, but pointed out that 1050 cm^{-1} for a bridging oxygen mode would be uniquely high. The Raman spectrum showed a very strong band at 1058 cm^{-1} . Since the band from a bridging linear $\text{M} - \text{O} - \text{M}$ species, would be expected to be at most weak, they concluded that the structure contained terminal oxygens and was therefore disordered.

The disorder of oxygen and fluorine atoms is not without precedent in oxymetal fluoride systems. In the cesium salt of CrO_3F^- , the anion occupies a position with site symmetry S_4 and only one bond length of $1.53\text{ \AA}$ is observed for the weighted average of $\text{Cr} = \text{O}$ and $\text{Cr} - \text{F}$ distances.

All the data can be interpreted by a disorder of two orientations of an asymmetrically fluorine-bridged structure, 15 and 16. The idealized symmetry of the tetrameric unit is $\sim\sim$



15
 $\sim\sim$



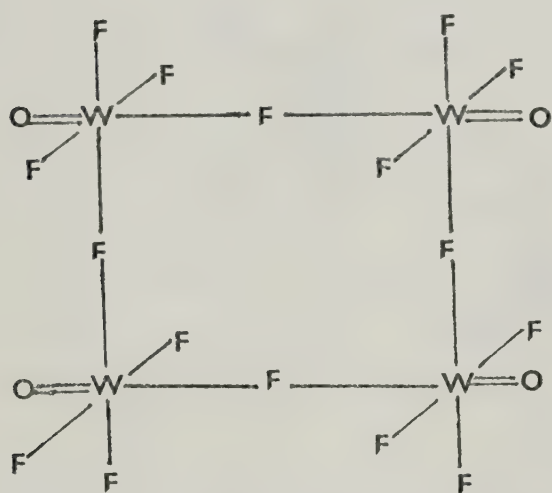
16
 $\sim\sim$

then C_{4h} .

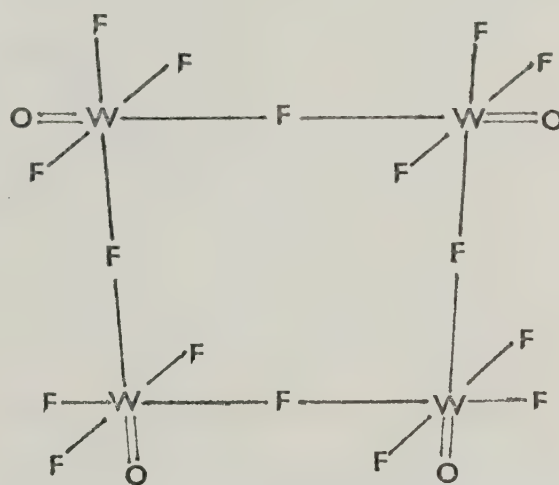
The relative merits of oxygen and fluorine bridged structures can be evaluated on the basis of expected bond lengths. A simple symmetry-based molecular orbital treatment of the oxygen-bridged structure shows that one might expect significant π bonding and hence a short tungsten-oxygen distance. The molecular orbitals, after construction of the σ framework can be briefly described as follows for the D_{4h} oxygen-bridge model. Along each edge of the square array perpendicular to the plane of the four metal atoms, a three centre W - O - W π -bonding system, consisting of a $d\pi$ orbital from each metal and the corresponding oxygen $p\pi$ orbital, would result in bonding, nonbonding and antibonding orbitals. Two electrons, those on the oxygen, are available to populate the bonding levels, thus giving an out of plane π -bond order of 0.5. In the plane, a more extensively delocalisation system results. The metal $d\pi$ orbitals transform as $A_{1g} + B_{2g} + Eu$ and the oxygen $p\pi$ orbitals as $A_{1g} + B_{1g} + Eu$. The metal and oxygen A_{1g} and Eu orbitals give rise to bonding and antibonding combinations of each symmetry. The eight available electrons are housed in the A_{1g} and Eu bonding orbitals and the B_{1g} non bonding orbital (which remains localised on the oxygen atoms). Thus a total in plane π -bond order of 3 is distributed among the eight equivalent W - O linkages. The total $\sigma + \pi$ bond order is therefore 1.875 for each metal-oxygen bond. The approximate bond order vs. bond length curve of

Cotton and Wing¹⁵⁵ would suggest a W - O bond length of 1.8 Å, assuming that W - O distances parallel Mo - O distances. However the observed W - 'O' distances are 2.10 and 2.12 Å which correspond to a bond order of 1.0.

Simple electron counting for a fluorine bridged structure suggest one oxygen per tungsten atom, and the pattern of in-plane and out-of-plane tungsten-ligand bond lengths¹⁵² suggest that the oxygen atoms lie in the plane of the four tungsten atoms, since it is in the plane that the rather short W - 'F' distances of 1.65 Å occur. These requirements allow three structures 15, 17 and 18.



17
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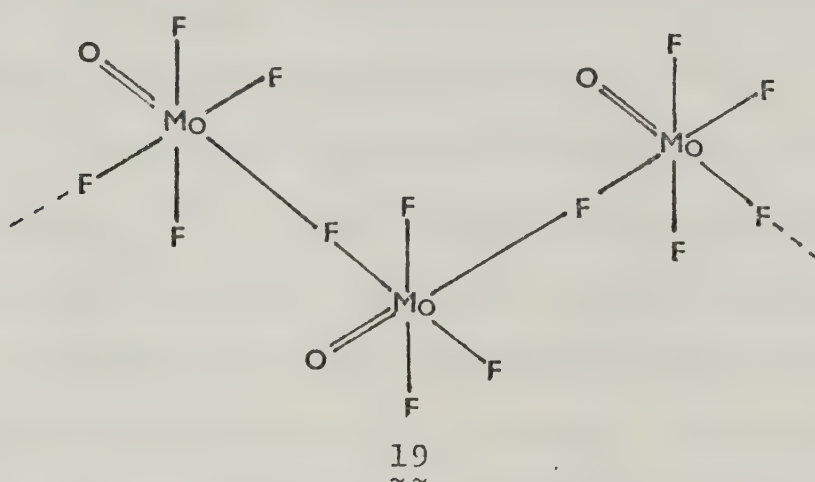


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The particular arrangement of the tungsten atoms in this structure requires either or both of the diagonals to be coincident with symmetry elements, depending upon the choice of space group C₂, C_m or C_{2/m}. Since none of these structures has a mirror plane that contains the diagonal tungsten atoms, a disorder and hence the presence of a pseudo symmetry element

has to be postulated in each case. Structure 15 is preferred over 17 and 18 because the disorder is based on a square, while 17 and 18 would probably contain a rectangle or trapezoid of tungsten atoms respectively.

The apparent W - F bridge distance, where the fluorine atom is placed at a position corresponding to the average of structures 15 and 16, can be readily assessed from the structure of MoOF_4 ¹⁵⁶. This structure forms infinite chains rather than the discrete tetrameric units found in WOF_4 . However, the essential heavy atom environments are the same as shown in 19.



The average of the two independent Mo - F distances (1.96 and 2.27) in this asymmetrically bridged structure is $2.11 \overset{\circ}{\text{Å}}$, the same as is found for bridge bonds in the tungsten compound.

The hypothesis of the disordered structure was then tested using the published structure factor amplitudes. Two models were refined: (a) the ordered oxygen bridged structure 14 and (b) an average of structure 15 and 16 with two indepen-

dent half weight fluorine atoms in each bridge, the terminal in plane atoms each being treated as a single atom comprising half oxygen and half fluorine. Both models were refined isotropically in the space group C2/m using scattering factors that contained the real and imaginary components of anomalous dispersion and the weighting scheme of Edwards and Jones. In model (b), only one half weight fluorine was refined in each cycle because of the resolution limits of the data set.

Both models refined to R factors of 0.126. The refinement of the disordered model produced asymmetric bridges with individual tungsten-fluorine distances 2.04 (7) and 2.19 (7). The other values were not significantly different from those observed by Edwards and Jones.

The X-ray data do not allow the rejection of the ordered model 14⁴⁴. This is not surprising in view of the quality of the data used and the relative insensitivity of the structure factors to small changes in the light atoms when a third row transition metal is present. Therefore the choice between the ordered and disordered models has to be made on the basis of other evidence. In this case the spectroscopic and structural arguments favour a fluorine bridged structure of which 15 is the most attractive.

References

1. W.R. Busing and H.A. Levy, *Acta Cryst.*, 10, 180 (1957).
2. A.L. Patterson, *Phys. Rev.*, 46, 372 (1934).
3. A.L. Patterson, *Z. Krist.*, A90, 517 (1935).
4. D. Harker, *J. Chem. Phys.*, 4, 381 (1936).
5. D. Harker and J.S. Kasper, *Acta Cryst.*, 1, 70 (1948).
6. D. Sayre, *Acta Cryst.*, 5, 60 (1952).
7. H. Hauptmann and J. Karle, *Acta Cryst.*, 3, 181 (1950).
8. H. Hauptmann and J. Karle, 'Solution to the Phase Problem I. The Centrosymmetric Crystal', A.C.A. Monograph No. 3 (1953).
9. M.M. Woolfson, *Acta Cryst.*, 7, 61 (1954).
10. W. Cochran and M.M. Woolfson, *Acta Cryst.*, 8, 1 (1955).
11. J. Karle and H. Hauptmann, *Acta Cryst.*, 9, 635 (1956).
12. J. Karle and I.L. Karle, *Acta Cryst.*, 21, 849 (1966).
13. H. Hauptmann and J. Karle, *Acta Cryst.*, 9, 45 (1956).
14. J.A. McCleverty, *Progress in Inorganic Chemistry*, 10, 49 (1968).
15. R. Eisenberg, *Progress in Inorganic Chemistry*, 12, 295 (1970).
16. G.N. Schrauzer and V.P. Mayweg, *J. Amer. Chem. Soc.*, 84, 3221 (1962).
17. H.B. Gray, R. Williams, I. Bernal and E. Billig, *J. Amer. Chem. Soc.*, 84, 4756 (1962).
18. J.D. Forrester, A. Zalkin and D.H. Templeton, *Inorg. Chem.*, 3, 1507 (1964).

19. R. Eisenberg and J.A. Ibers, R.J.H. Clark and H.B. Gray, J. Amer. Chem. Soc., 86, 113 (1964).
20. R. Eisenberg and J.A. Ibers, Inorg. Chem., 4, 605 (1965).
21. C.J. Fritchie, Jr., Acta Cryst., 20, 107 (1966).
22. D. Sartain and M.R. Truter, Chem. Commun., 1382 (1966).
23. D. Sartain and M.R. Truter, J. Chem. Soc., A, 1264 (1967).
24. J.D. Forrester, A. Zalkin and D.H. Templeton, Inorg. Chem., 3, 1500 (1964).
25. J.H. Enemark and J.A. Ibers, Inorg. Chem., 7, 2636 (1968).
26. R. Eisenberg, Z. Dori, H.B. Gray and J.A. Ibers, Inorg. Chem., 7, 741 (1968).
27. A. Davison N. Edelstein, R.H. Holm and A.H. Maki, J. Amer. Chem. Soc., 85, 2029 (1963).
28. R. Eisenberg and J.A. Ibers, J. Amer. Chem. Soc., 87, 3776 (1965).
29. R. Eisenberg and J.A. Ibers, Inorg. Chem., 5, 411 (1966).
30. A.E. Smith, G.N. Schrauzer, V.P. Mayweg and W. Heinrich, J. Amer. Chem. Soc., 87, 5798 (1965).
31. R. Eisenberg, E.I. Stiefel, R.C. Rosenberg and H.B. Gray, J. Amer. Chem. Soc., 88, 2874 (1966).
32. R. Eisenberg and H.B. Gray, Inorg. Chem., 6, 1844 (1967).
33. A. Davison, N.E. Edelstein, R.H. Holm and A.H. Maki, J. Amer. Chem. Soc., 86, 2799 (1964).
34. J.H. Waters, R. Williams, H.B. Gray, G.N. Schrauzer and H.W. Frick, J. Amer. Chem. Soc., 86, 4198 (1964).
35. E.I. Stiefel, Z. Dori and H.B. Gray, J. Amer. Chem. Soc., 89, 3353 (1967).

36. J. Locke, J.A. McCleverty, E.J. Wharton and C.J. Winscom, Chem. Commun., 677 (1966).
37. J. Locke, J.A. McCleverty, E.J. Wharton and C.J. Winscom, Chem. Commun, 1289 (1967).
38. J.A. McCleverty, N.M. Atherton, J. Locke, E.J. Wharton and C.J. Winscom, J. Amer. Chem. Soc., 89, 6082 (1967).
39. T. Birchall, N.N. Greenwood, J.A. McCleverty, Nature, 215, 625 (1967).
40. T. Birchall and N.N. Greenwood, J. Chem. Soc., A, 286 (1969).
41. A.L. Patterson and W.E. Love, Amer. Min., 45, 325 (1960).
42. D.T. Cromer, Acta Cryst., A24, 321 (1968).
43. R. Mason and G.B. Robertson, in Advances in Structure Research by Diffraction Methods, vol 2, R. Brill and R. Mason (Eds.), Interscience Division, Wiley, New York (1966).
44. W.C. Hamilton, Acta Cryst., 18, 502 (1965).
45. R.P. Dodge and V. Schomaker, J. Organometal. Chem., 3, 274 (1965).
46. L.F. Dahl, E.R. deGil and R.D. Feltham, J. Amer. Chem. Soc., 91, 1653 (1969).
47. W.C. Hamilton and I. Bernal, Inorg. Chem., 6, 2003 (1967).
48. A.I.M. Rae, Chem. Communs., 1245 (1967).
49. F. Epstein and I. Bernal, Chem. Communs., 136 (1970).
50. D.J. Hodgson and J.A. Ibers, Inorg. Chem., 11, 2345 (1968).
51. M. Colapietro, A. Domenicano, L. Scarramuzza, A. Vaciago and L. Zambonelli, Chem. Communs. 583 (1967).

52. P.T. Manoharan and W.C. Hamilton, *Inorg. Chem.*, 2, 1043 (1963).
53. G.P. Khare and R. Eisenberg, *Inorg. Chem.*, 11, 1385 (1972).
54. A. Butcher and P.C.H. Mitchell, *Chem. Commun.*, 176 (1967).
55. N.G. Connelly and J.A. McCleverty, *J. Chem. Soc. A*, 1621 (1970).
56. M.J. Bennett, J.T. Purdham, S. Takada and S. Masamune, *J. Amer. Chem. Soc.*, 93, 4063 (1971).
57. H.D. Stidham, *Spectrochim. Acta*, 21, 23 (1965).
58. H. Gerding and F.A. Haak, *Rec. Trav. Chim.*, 68, 293 (1949).
59. B.J. Monostori and A. Weber, *J. of Mol. Spectry.*, 12, 129 (1964).
60. J. Laane and R.C. Lord, *J. of Mol. Spectry.*, 39, 340 (1971)
61. Ichiro Miyagawa, Yanezo Mornio and R. Riemschneider, *Bull. Chem. Soc., Japan*, 27, 177 (1954).
62. W.D. Kumler, R. Boikess, P. Bruck and S. Winstein, *J. Amer. Chem. Soc.*, 86, 3126 (1964).
63. F.H. Herbststein, *J. Chem. Soc.*, 2292 (1959).
64. G. Favini, F. Zuccarello and G. Buemi, *J. Mol. Struct.*, 3, 385 (1969).
65. G. Dallinga and L.H. Toneman, *J. Mol. Struct.*, 1, 117 (1967).
66. H. Oberhammer and S.H. Bauer, *J. Amer. Chem. Soc.*, 91, 10 (1969).
67. P. Ganis, C. Pedone, P.A. Temussi, *Atti. Accad. Nazion. Lincei R.C.Cl. Sci. Fis. Mat. Nat.*, 35, 68 (1963).

68. P. Ganis, C. Pedone, P.A. Temussi, Atti. Accad. Nazion. Lincei R.C. Cl. Sci. Fis. Mat. Nat., 35, 175 (1963).
69. R.J. Jandacek and S.H. Simonsen, J. Amer. Chem. Soc., 91, 6663 (1969).
70. P.W.R. Corfield, R.J. Doedens and J.A. Ibers, Inorg. Chem., 6, 197 (1967).
71. G. Germain and M.M. Woolfson, Acta Cryst., B, 24, 91 (1968).
72. W.H. Zacharisen, Acta Cryst., 16, 1139 (1963).
73. C. Pedone, E. Benedetti, A. Immirzi and G. Allegra, J. Amer. Chem. Soc., 92, 3549 (1970).
74. J.F. Chiang and S.H. Bauer, J. Amer. Chem. Soc., 91, 1898 (1969).
75. K. Sasvári and M. Löw, Acta Cryst., 19, 840 (1969).
76. D.P. Shoemaker, H. Kindler, W.G. Sly and R.C. Strivastova, J. Amer. Chem. Soc., 87, 482 (1965).
77. P.J. Wheatley, J. Chem. Soc., 3136 (1965).
78. W.R. Roth, W.B. Bang, P. Goebel, R.L. Sass, R.B. Turner, A.P. Yü, J. Amer. Chem. Soc., 86, 3178 (1964).
79. B.T. Kilbourn and P.G. Owston, J. Chem. Soc., B, 1 (1970).
80. H.R. Harrison, O.J.R. Hodder and D.C. Hodgkin, J. Chem. Soc., B, 640 (1971).
81. T. Sato and H. Koyama, J. Chem., Soc., B, 1070 (1971).
82. G. Casalone and M. Simonetta, J. Chem. Soc., B, 1180 (1971).
83. G.S. Pawley, W.N. Lipscomb and H.H. Freedman, J. Amer. Chem. Soc., 86, 4725 (1964).

84. J.C.J. Bart, *Acta Cryst.*, B, 24, 1277 (1968).
85. L. Leiserowitz and G.M.J. Schmidt, *Acta Cryst.*, 18, 1058 (1965).
86. J.D. Dunitz and P. Strickler, *Helv. Chem. Acta.*, 49, 2505 (1966).
87. J.D. Dunitz and P. Strickler, "Preferred Conformation of the Carboxyl Group", in "Structural Chemistry and Molecular Biology", A. Rich and N. Davidson (Eds.), W.H. Freeman and Co., San Francisco and London (1968).
88. J.P. Schaefer and C.R. Costin, *J. Org. Chem.*, 33, 1677 (1968).
89. M. Sundralingam and L.H. Jensen, *Acta Cryst.*, 18, 1053 (1965).
90. P.J. Wheatley, *J. Chem. Soc.*, 6036 (1964).
91. T.N. Margulis and M.S. Fischer, *J. Amer. Chem. Soc.*, 89, 223 (1967).
92. E. Benedetti, P. Corradini, C. Pedone, and B. Post, *J. Amer. Chem. Soc.*, 91, 4072 (1969).
93. B.L. Barnett and R.F. Davis, *Acta Cryst.*, B, 26, 326 (1970).
94. S.T. Rao and M. Sundralingam, *J. Amer. Chem. Soc.*, 92, 4963 (1970).
95. A. McL. Mathieson, *Tetrahedron Letts.* no. 46 4137 (1965).
96. H.H. Stechl, *Chem. Ber.*, 97, 2681 (1964).
97. N. Obata and I. Moritani, *Bull. Chem. Soc. Japan*, 39, 2250 (1966).
98. C. Deboer and R. Breslow, *Tetrahedron Lett.*, 11, 1033 (1967).

99. H. Dürr, *Tetrahedron Lett.*, 17, 1649 (1967).
100. E.L. Allred, J.C. Hinshaw, *J. Amer. Chem. Soc.*, 90, 6885 (1968).
101. H. Tanida, S. Teretake, *Tetrahedron Lett.*, 57, 4991 (1970).
102. J. Schipperijn and J. Lukas, *Tetrahedron Lett.*, 3, 231 (1972).
103. B.L. Barnett and R.E. Davis, *Acta Cryst.*, B, 26, 1026 (1970).
104. O. Bastiansen, F.N. Fritsch and K. Hedberg, *Acta Cryst.*, 17, 538 (1964).
105. A. Bhaumik, W.V.F. Brooks, S.C. Dass and K.V.L.N. Sastry, *Can. J. Chem.*, 48, 2949 (1970).
106. R.E. Long, H. Maddox and K.N. Trueblood, *Acta Cryst.*, B, 25, 2083 (1969).
107. A. Hartman and F.L. Hirshfeld, *Acta Cryst.*, 20, 80 (1966).
108. R.H. Schwendeman, G.D. Jacobs and T.M. Krigas, *J. Chem. Phys.*, 40, 1022 (1966).
109. J. Eraker, C.H.R. Rømming, *Acta Chem. Scand.*, 21, 2721 (1967).
110. C. Jongsmer and H. Van der Meer, *Recl. Trav. Chim. Pays-Bas*, 90, 33 (1971).
111. F.P. Boer, J.J. Flynn and J.K. Hecht, *J. Chem. Soc.*, B, 381 (1970).
112. W.J. Jones and B.P. Stoicheff, *Can. J. Phys.*, 42, 2259 (1964).
113. L.S. Bartell and J.P. Guillory, *J. Chem. Phys.*, 43, 647 (1965).

- 114. C.J. Fritchie, *Acta Cryst.*, 20, 27 (1966).
- 115. F.R. Ahmed and E.J. Gabe, *Acta Cryst.*, 17, 603 (1964).
- 116. J. Trotter, C.S. Gibbons, N. Nakatsuka and S. Masamune, *J. Amer. Chem. Soc.*, 89, 2792 (1967).
- 117. C.S. Gibbons and J. Trotter, *J. Chem. Soc. A*, 2027 (1967).
- 118. R.D. Suenram and M.D. Harmony, *J. Chem. Phys.*, 56, 3837 (1972).
- 119. A. Almenningen, O. Bastiansen and P.N. Skancke, *Acta Chem. Scand.*, 15, 711 (1961).
- 120. R.C. Lord and B.P. Stoicheff, *Can. J. Phys.*, 40, 711 (1962).
- 121. E. Benedetti, P. Corradini and C. Pedone, *Acta Cryst.*, B, 26, 493 (1970).
- 122. E. Adman and T.N. Margulis, *J. Phys. Chem.*, 73, 1480 (1969).
- 123. E. Adman and T.N. Margulis, *J. Amer. Chem. Soc.*, 90, 4517 (1968).
- 124. I.L. Karle, J. Karle and K. Britts, *J. Amer. Chem. Soc.*, 88, 2918 (1966).
- 125. B. Greenberg and B. Post, *Acta Cryst.*, B, 24, 918 (1968).
- 126. C.M. Bock, *J. Amer. Chem. Soc.*, 90, 2748 (1968).
- 127. T.N. Margulis, *J. Amer. Chem. Soc.*, 93, 2193 (1971).
- 128. T.N. Margulis, *J. Chem. Soc., D*, 215 (1969).
- 129. C.H. Chiang, R.F. Porter and S.H. Bauer, *J. Mol. Struct.*, 7, 89 (1971).
- 130. W.J. Adams and L.S. Bartell, *J. Mol. Struct.*, 8, 199 (1971).
- 131. J.D. Dunitz, *Acta Cryst.*, 2, 1 (1949).
- 132. E.B. Fleischer, *J. Amer. Chem. Soc.*, 86, 3889 (1964).

- 133. N. Camerman, D. Weinblum and S.C. Nyburg, J. Amer. Chem. Soc., 91, 982 (1969).
- 134. N. Camerman and S.C. Nyburg, Acta Cryst., B, 25, 388 (1970).
- 135. T.N. Margulis, Acta Cryst., 18, 742 (1965).
- 136. E. Adman, M.P. Gordon and L.H. Jensen, Chem. Commun., 1019 (1969).
- 137. J.R. Einstein, J.L. Hosszu, J.W. Longworth, R.O. Rahn and C.H. Wei, Chem. Commun., 1063 (1967).
- 138. P.R. Brook, A.J. Duke and J.R. Duke, J. Chem. Soc., D, 574 (1970).
- 139. B.L. Barnett and R.E. Davis, Acta Cryst., B, 26, 1026 (1970).
- 140. H.A. Bent, Chem. Reviews, 61, 275 (1961).
- 141. M.J.S. Dewar, Tetrahedron, 1817 (1965).
- 142. K.W. Cox and M.D. Harmony, J. Chem. Phys., 50, 1976 (1969).
- 143. J.F. Chiang and S.H. Bauer, J. Amer. Chem. Soc., 92, 1614 (1970).
- 144. K.W. Cox and M.D. Harmony, J. Mol. Spectry., 36, 34 (1970).
- 145. R.H. Hoffmann, Tetrahedron Lett., 33, 2907 (1970).
- 146. R.H. Hoffmann and R.B. Davidson, J. Amer. Chem. Soc., 93, 5699 (1971).
- 147. J.F. Chiang, J. Amer. Chem. Soc., 93, 5044 (1971).
- 148. G. Dallinga and L.H. Toneman, Recl. Trav. Chim. Pays-Bas, 86, 171 (1967).

149. R. Bellomo, R. Destro, C.M. Gramaccioli and M. Simonetta, J. Chem. Soc., B, 710 (1969).
150. R. Vukov, Ph.D. Thesis.
151. Y. Tsukada, T.Sato, M. Shiro and H. Koyama, J. Chem. Soc., B, 1166 (1971).
152. A.J. Edwards and G.R. Jones, J. Chem. Soc., A, 2074 (1968).
153. I.R. Beattie and D.J. Reynolds, Chem. Commun., 1531 (1968).
154. I.R. Beattie, K.M.S. Livingston, D.J. Reynolds and G.A. Ozin, J. Chem. Soc., A, 1210 (1970).
155. F.A. Cotton and R.M. Wing, Inorg. Chem., 4, 867 (1965).
156. A.J. Edwards, B.R. Steventon, J. Chem. Soc., A, 2503 (1968).

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